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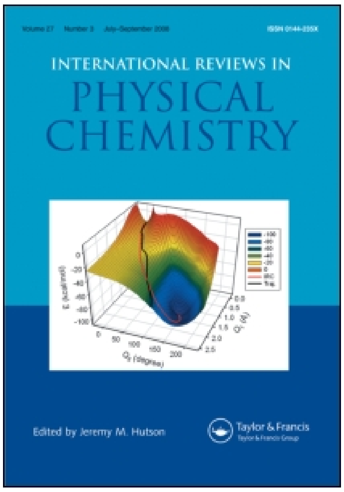

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Hyperspherical harmonics as Sturmian orbitals in momentum space: a systematic approach to the few-body Coulomb problem

VINCENZO AQUILANTI, SIMONETTA CAVALLI, CECILIA COLETTI,
DANIELA DI DOMENICO and GAIA GROSSI
Dipartimento di Chimica, Università di Perugia, I-06123 Perugia, Italy

To exploit hyperspherical harmonics (including orthogonal transformations) as basis sets to obtain *atomic and molecular orbitals*, Fock projection into momentum space for the hydrogen atom is extended to the mathematical d-dimensional case, higher than the physical case $d = 3$. For a system of N particles interacting through Coulomb forces, this method allows us to work both in a $d = 3(N-1)$ dimensional configuration space (on eigenfunctions expanded on a Sturmian basis) and in momentum space (using a $(d+1)$-dimensional hyperspherical harmonics basis set). Numerical examples for three-body problems are presented. Performances of alternative basis sets corresponding to different coupling schemes for hyperspherical harmonics have also been explicitly obtained for bielectronic atoms and H_2^+ (in the latter case, also in the Born–Oppenheimer approximation extending the multicentre technique of Shibuya and Wulfman). Among the various generalizations and applications particularly relevant is the introduction of alternative expansions for multidimensional plane waves, of use for the generalization of Fourier transforms to many-electron multicentre problems. The material presented in this paper provides the starting point for numerical applications, which include various generalizations and hierarchies of approximation schemes, here briefly reviewed.

Contents

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1. Introduction

1.1. *Motivation*

In this paper we deal with atomic and molecular structure as a quantum mechanical few-body problem: properly normalized hyperspherical harmonics (here appearing as Fourier transforms of hydrogenic Sturmians [1, 2]) are considered as expansion basis sets for atomic and molecular orbitals. In the treatment presented a key role is played by the famous Fock projection for the hydrogen atom in momentum space, which leads to the connection between hydrogenic orbitals and hyperspherical harmonics on the four-dimensional sphere S^3. Since these harmonics are a basis set for the irreducible representations of the rotation group in a four-dimensional space, hydrogenoid orbitals can be looked at as representations of the four-dimensional hyperspherical symmetry [3].

Harmonic analysis is a basic tool for quantum chemistry and atomic and molecular physics. It generalizes Fourier expansions and transforms, and its computational implementation is now being extended beyond the three-dimensional case [3, 4]. In quantum mechanics, wavefunctions for the angular part of the kinetic energy operator are spherical harmonics, that is eigensolutions to the Beltrami–Laplace operator on the ordinary sphere: they add and multiply according to the rotation group operations, so providing the framework for the quantum theory of angular momentum (Clebsch–Gordan series, sum rules for 3-j and 6-j coefficients, . . .). For few-body dynamics, the kinetic energy operators, when conveniently written in *hyperspherical coordinates*, can be added so as to give a Beltrami–Laplace operator on a multidimensional sphere: its eigensolutions are *hyperspherical harmonics*, which can be interpreted as wavefunctions of *hyperangular momenta*, whose algebra can be developed, within the framework of orthogonal polynomial and hypergeometric function theory [5].

Hyperspherical coordinates for mapping of potential energy surface are well established for three-body problems and the use of harmonics as expansion basis sets as well. Progress for problems involving more particles is recorded in nuclear, atomic and molecular physics, leading to interesting mathematical and computational implications: examples are generalizations [6] of 3-j and 6-j coefficients and their connections with Hahn's and Racah's discrete polynomials. These connections are particularly illuminating also because they allow handling through algebraic codes.

These techniques involve, for the N-body problem, the introduction of a hypersphere of dimensionality $3N-4$, and the additional variable, the hyperradius ρ, is treated on a different footing. This is useful in general and crucial for reactions. Although we exploit many of the technicalities of the current approach, we work on a $3N-3$ sphere, that is we map all the coordinates on hyperspheres of unit radius, but we do this in momentum space and for structural problems.

This paper is intended essentially as a guided tour on setting up a formulation of the problem of quantum chemistry (atomic and molecular structure) as a perturbation of the hyperspherical symmetry, and thus most parts have the character of a review. However, we believe that the emphasis on harmonic expansions and the extended angular momentum algebra has the flavour of novelty, as the consideration of alternative coordinates and coupling schemes for the three-body problem. For progress on four bodies, see [7–12].

New results are as follows.

(i) The expression of the secular equations entirely in terms of ingredients of (extended) angular momentum algebra (see section 3.2). This is shown here to be feasible also for 'radial' integrals. This allows the understanding of the structure of the relevant matrices, including their zeroes, sparseness being crucial in applications.

(ii) The alternative formulations of the three-body Coulomb problem, including numerical results both for the isoelectronic sequence and for different mass combinations, particularly H_2^+ [2]. The latter example proves the variational convergence of the procedure, previously questioned [13].

1.2. *Background*

In 1935 Fock [14] proved that the wavefunctions of the hydrogen atom $|nlm\rangle$ in momentum space are, apart from a normalization factor, four-dimensional spherical harmonics, that is eigenfunctions of the Laplace operator on the three-dimensional manifold S^3 (the surface of the sphere embedded in a four-dimensional Euclidean space). Thus the *principal quantum number n* can appropriately be interpreted as a *hyperangular momentum* quantum number: the *hidden symmetry* giving rise to the *accidental degeneracy* emerging in the three-dimensional configuration space treatment is actually a manifestation of a symmetry in four-dimensional space. Such a symmetry has been analysed and discussed in various papers [15], reviews [16] and books [17]. The $|nlm\rangle$ basis, which will be referred to as *spherical* in the following, corresponds to separation in polar coordinates, and in momentum space to separation in spherical coordinates on the hypersphere S^3 [18]. As an alternative to the $|nlm\rangle$ basis, it is also interesting to consider in detail the *Stark* and *Zeeman* bases which are particularly useful in problems where a direction in space is privileged, such as is the case when atoms are in an electric or magnetic field. The *Stark* states $|n\mu m\rangle$ correspond to separation in parabolic coordinates on ordinary space and in cylindrical coordinates on S^3. The *Zeeman* basis, denoted as $|n\lambda m\rangle$, has been introduced more recently by Labarthe [19] and has found increasing applications [20]. According to the emerging interpretation of the quantum numbers, the passage between the alternative sets can be explicitly viewed as a change in coupling schemes of hyperangular momenta [21].

The generalization of Fock's projection to higher spaces permits multielectronic and multicentre orbitals to be built up. Six-dimensional Sturmian functions and their counterparts in momentum space, seven-dimensional hyperspherical harmonics—that is bases for the irreducible representations of the rotational group $O(7)$—are considered as basis sets to expand atomic orbitals for bielectronic systems (helium and its isoelectronic series). The advantage of employing hyperspherical harmonics lies in the possibility of introducing alternative parametrizations, labelled by various quantum numbers, corresponding to different reduction schemes of the rotational group $O(7)$ into its subgroups. The approach is completely general and formally can be extended to any N-body Coulomb problem; the matrix elements which have to be calculated for the secular equation, are expressed by vector coupling and recoupling coefficients (harmonic superpositions) of the rotation group $O(d)$, since in the expansions d-dimensional hyperspherical harmonics are used. Since these coefficients coincide with those of angular momentum algebra conveniently generalized, this compact formalism is interpretable in terms of couplings and recouplings of hyperangular momenta. This leads to a classification of hyperspherical bielectronic orbitals, here given explicitly for zero total angular momentum. The effectiveness of the various parametrizations are illustrated according to the physical interpretation attached to the meaning of the different quantum numbers.

1.3. *Outline*

Section 2 accounts for the hyperspherical harmonics of the four-dimensional rotation group $O(4)$ according to the same spirit of previous investigations [2, 4], where the possibility has been considered of exploiting different parametrizations of the S^n hypersphere to build up alternative Sturmian [22] basis sets. Their symmetry and completeness properties make them in fact adapt to solve quantum mechanical problems where, although the hyperspherical symmetry of the kinetic energy operator is broken by the interaction potential, the corresponding perturbation matrix elements can be worked out explicitly: this is the case of many particles interacting through Coulomb forces (see section 3). Section 4 includes numerical tables and appraisals of the convergence for the key example of three Coulomb particles, in particular for the two electron systems of the He sequence.

Generalizations [22, 23] greatly improving convergence and extension to molecules within the fixed-nuclei scheme [2] are under focus. Section 5 provides additional remarks and concludes the paper by indicating directions of further progress.

2. Hydrogenic orbitals and the symmetry of the hypersphere S^3

In section 2.1 we review the Fock projection onto the surface of a sphere in four-dimensional hyperspace in order to establish the connections of the momentum space wavefunctions with hyperspherical harmonics. In particular, the relationships among coordinate sets which define the spherical, the Stark and the Zeeman basis sets are considered. The explicit formulae for transformations between these bases are given in section 2.2.

In some preceding papers [5, 24] we have indicated how to exploit the fact that in the theory of the $O(4)$ group [17], the 3-sphere admits different systems of hyperspherical coordinates to which correspond alternative harmonics. In [3] we have classified the hyperspherical harmonics of the group $O(4)$, and shown that there are 15 distinct bases. The relationship between alternative separable solutions of the Coulomb problem in momentum space is exploited in order to obtain hydrogenic orbitals that are of interest for Sturmian expansions of use in atomic and molecular structure calculations and for the description of atoms in fields.

2.1. *Momentum space: alternative hydrogenic orbitals*

That Sturmian eigenfunctions in momentum space in spherical coordinates are, apart from a weight factor, standard hyperspherical harmonics (see equation (9)), can be seen following the famous Fock treatment of the hydrogen atom in which the tridimensional space is projected onto the 3-sphere S^3 (the unit radius hypersphere embedded in a four-dimensional space). The essentials of Fock analysis of relevance here are briefly sketched now.

The Fock transformation of variables consists in projecting the momentum vector **p** with coordinates p_x, p_y, p_z and modulus p on a tetradimensional hypersphere. This transformation is analogous to the inverse of a stereographic projection: each point on the 3-sphere with coordinates u_1, u_2, u_3, u_4 corresponds to the point p_x, p_y, p_z:

$$\begin{aligned} u_1 &= \frac{2p_0 p_y}{p_0^2 + p^2} = \sin\chi \sin\vartheta \sin\varphi \\ u_2 &= \frac{2p_0 p_x}{p_0^2 + p^2} = \sin\chi \sin\vartheta \cos\varphi \\ u_3 &= \frac{2p_0 p_z}{p_0^2 + p^2} = \sin\chi \cos\vartheta \\ u_4 &= \frac{p_0^2 - p^2}{p_0^2 + p^2} = \cos\chi \end{aligned} \tag{1}$$

where the momentum $p_0 = (-2E)^{1/2}$ is directly related to the energy spectrum. Here u_1, u_2, u_3, u_4 define a hypersphere of unit radius

$$u_1^2 + u_2^2 + u_3^2 + u_4^2 = 1 \tag{2}$$

and the polar angles ϑ and φ specify the orientation of the vector **p** in momentum space:

$$\begin{aligned} p_x &= p \sin\vartheta \cos\varphi \\ p_y &= p \sin\vartheta \sin\varphi \\ p_z &= p \cos\vartheta. \end{aligned} \tag{3}$$

The spherical parametrization (1)—graphically exhibited by the tree method [24] (see figure 1(*a*))—is used to establish the relationship between the volume element d**p** in momentum space and the solid angle element dω in the four-dimensional space:

$$\mathrm{d}\mathbf{p} = \left(\frac{p_0^2 + p^2}{2p_0}\right)^3 \mathrm{d}\omega \tag{4}$$

where

$$\mathrm{d}\mathbf{p} = p^2\, \mathrm{d}p \sin\vartheta\, \mathrm{d}\vartheta\, \mathrm{d}\varphi \tag{5}$$

and

$$\mathrm{d}\omega = \sin^2\chi \sin\vartheta\, \mathrm{d}\chi\, \mathrm{d}\vartheta\, \mathrm{d}\varphi \tag{6}$$

being that (from equation (1)):

$$\frac{\mathrm{d}\chi}{\mathrm{d}p} = \frac{2p_0}{p_0^2 + p^2}. \tag{7}$$

In order to illustrate graphically the geometrical interpretation of Fock's transformation we refer to a two-dimensional momentum space (the plane (p_1, p_2)). Figure 2 illustrates the inverse stereographic projection p_1, p_2 of a point u_1, u_2, u_3 on the surface of a unit radius sphere S^2 in the familiar three-dimensional space.

In the specific case of the hydrogen atom the eigenfunctions $\psi_{nlm}(\mathbf{p})$ in momentum space, which can be considered as Fourier transforms of their configuration space counterparts:

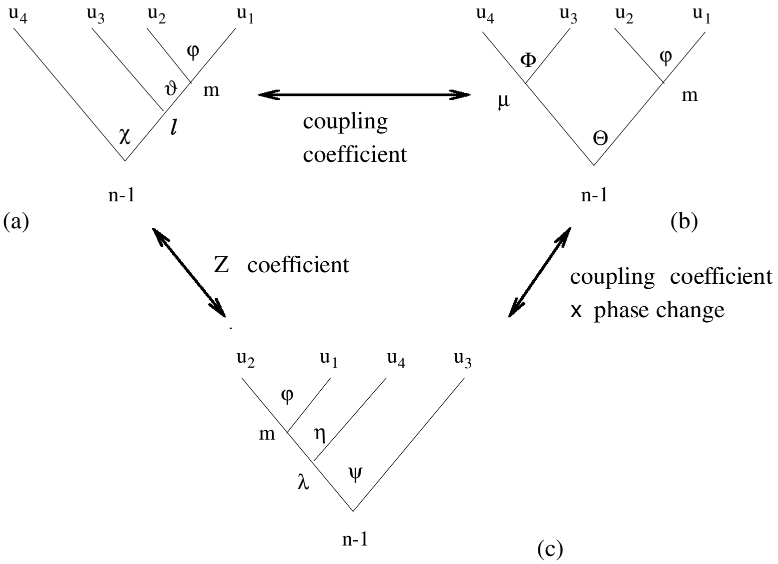


Figure 1. Three alternative parametrizations of the unit sphere S^3 in the four-dimensional space R^4, corresponding to three different hyperspherical harmonics. The *tree* graphical technique [25–27] is employed: it illustrates the relationship between Cartesian coordinates u_i and angular parametrizations of the hypersphere. A hypersphere of R^4 is parametrized either by four Cartesian coordinates or by a hyperradius ρ and three hyperangles. There are four 'leaves' corresponding to the Cartesian coordinates, connected to the branches which join at three nodes representing the angles. The convention is as follows: the branch converging to the node from the left (right) represents the cosine (sine) of the hyperangles. Starting from a leaf and going down to the root of the tree, through the various nodes, we establish a relation between coordinates and hyperangles. Tree (*a*) shows Fock projection when the parametrization is according to the coordinate system (1) and the corresponding harmonics is $Y_{n-1,l,m}(\chi,\vartheta,\varphi)$. Tree (*b*) is an alternative representation with respect to tree (*a*); it corresponds to a parametrization according to the angles in equation (10). The corresponding harmonic is $(-)^{n-1}(\imath)^m(n/(2\pi^2))^{1/2}D^{(n-1)/2}_{(\mu+m)/2,(\mu-m)/2}(-\Phi-\varphi, 2\Theta, \varphi-\Phi)$. We can pass from tree *a* to *b* using the suitable Clebsch–Gordan coefficient (equation (12)). Tree (*c*) illustrates the hyperspherical parametrization that leads to the hyperspherical harmonics $Y_{n-1,\lambda,m}(\psi,\eta,\varphi)$. They are related to the harmonics of tree (*a*) through the *Z* coefficient defined in equation (13). The connection between (*b*) and (*c*) requires a Clebsch–Gordan coefficient and a phase change connected to α (see equation (14)). From a Lie group theoretical viewpoint, trees (*a*) and (*c*) correspond to $O(4) \supset O(3) \supset O(2)$, which is the chain of reduction of the four-dimensional rotation groups $O(3)$ and $O(2)$, respectively. Tree (*b*) corresponds to $O(4) \supset O(2) \times O(2)$.

$$\psi_{nlm}(\mathbf{p}) = (2\pi)^{-3/2}\int \exp(-\imath\mathbf{r}\cdot\ \mathbf{p})u_{nlm}(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{8}$$

are just hyperspherical harmonics except for a weight function. That is

$$\psi_{nlm}(\mathbf{p}) = (-)^{n-1-|m|}(\imath)^{l+m-|m|}\frac{4p_0^{5/2}}{(p_0^2+p^2)^2}\cdot Y_{n-1,l,m}(\chi,\vartheta,\varphi). \tag{9}$$

The explicit expressions for $\psi_{nlm}(\mathbf{p})$ for the hydrogen atom had been obtained for the first time by Podolsky and Pauling [28] analytically. Through the tree method [24]

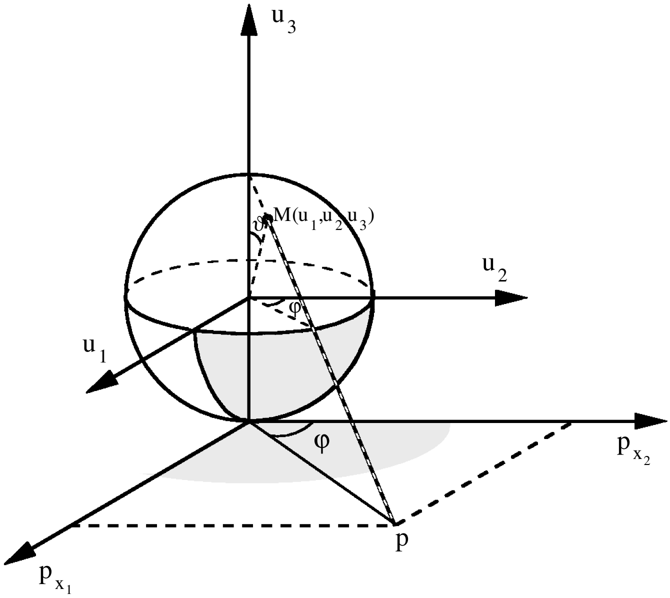


Figure 2. The stereographic projection establishes a relationship between points on a sphere S^n and a Euclidean space R^n. The case $n = 3$ is the one used by Fock for the hydrogen atom (see section 2). The simpler case $n = 2$ is shown here for illustration: stereographic projection of a point $\mathbf{p}$ in a plane with coordinates $p_1 = p \sin \varphi$ and $p_2 = p \cos \varphi$ onto the surface of a unit sphere with coordinates $u_1 = \sin \vartheta \sin \varphi$, $u_2 = \sin \vartheta \cos \varphi$, $u_3 = \cos \vartheta$, where $\cos \vartheta = (p_0^2 - p^2)/(p_0^2 + p^2)$. The shaded zone represents the projection of the points of the plane onto the part of the spherical bowl comprised between the equator and the axes u_1 and u_2. The points fulfilling the condition $p = p_0$ are projected onto the equator.

figure 1(*a*) shows that the part in m and l represents the spherical harmonic and the part in l and n a Gegenbauer polynomial. According to this point of view the quantum number n plays the role of a hyperangular momentum quantum number, labelling a harmonic on S^3.

The connections between alternative systems of hyperspherical coordinates are visualized by the tree method [24] in figure 1; from a group theoretical viewpoint, the alternative coupling schemes are seen to correspond to the subgroup reduction chains $O(4) \supset O(3) \supset O(2)$ (figures 1(*a*) and (*c*)) and $O(4) \supset O(2) \times O(2)$ (figure 1(*b*)). The figure also illustrates how alternative quantum numbers for the basis sets arise as labels for harmonics for the subgroups of the reduction chain.

Figure 1 also helps in writing down the four-dimensional sphere parametrizations corresponding to the alternative representations for Fock projection.

The set of angles in figure 1(*b*) parametrizing the 3-sphere defines a point on the three-dimensional sphere [17] as follows:

$$\begin{aligned} u_1 &= \sin \Theta \sin \varphi \\ u_2 &= \sin \Theta \cos \varphi \\ u_3 &= \cos \Theta \sin \Phi \\ u_4 &= \cos \Theta \cos \Phi \end{aligned} \tag{10}$$

where Θ, φ, Φ are the cylindrical angles describing the coordinates on a tetradimensional space (see also [17]; a similar system of angles is used by Kalnins *et al.* [15] who give a general treatment of the properties of the group $O(4)$).

Through the set of angles in figure 1(*c*), a point in the four-dimensional momentum space is defined in the following way:

$$\begin{aligned} u_1 &= \cos\psi\cos\eta\sin\varphi \\ u_2 &= \cos\psi\cos\eta\cos\varphi \\ u_3 &= \sin\psi \\ u_4 &= \cos\psi\sin\eta \end{aligned} \tag{11}$$

where ψ and η are the hyperangles that define the *Zeeman* basis.

2.2. *The connection between alternative basis sets*

In the following, we pay special attention to the connections among the spherical, Stark and Zeeman basis. Since in momentum space the orbitals are simply related to hyperspherical harmonics, these connections, strictly linked to alternative parametrizations of the 3-sphere illustrated in the previous section, are given by orthogonal matrix elements similar (when not identical) to the elements of angular momentum algebra.

Let us now consider the overlap between the spherical and the Stark basis. For the latter, the momentum space eigenfunctions, which in configuration space correspond to variable separation in parabolic coordinates, are similarly related to alternative hyperspherical harmonics [2]. The connecting coefficient between *spherical* and *Stark* basis is formally identical to a usual vector coupling coefficient (from now on n is omitted from the notation):

$$\langle lm|\mu m\rangle = (-)^{(n-1+m-\mu)/2}\left\langle \frac{n-1+m}{2}, -\frac{\mu}{2}; \frac{n-1-m}{2}, \frac{\mu}{2} \middle| l0 \right\rangle \tag{12}$$

for any allowed n, $n \geq l+1$ and $n \geq |m| + |\mu| + 1$. This transformation was given for the first time in configuration space by Park [29], who did not specify the explicit form of the eigenfunctions and so did not define the phase convention. Progress was made by Hughes [30] and by Tarter [31] (who calculated the matrix elements by direct integration) and the correct phase is given by Englefield [17]. Note that for the basis set $|\mu m\rangle$, unlike $|lm\rangle$, the operation of parity is not conserved, however, it is possible to build a parity conserving Stark basis set by appropriately combining the basis functions $|\mu m\rangle$. Progress in this sense is described in [32].

The Clebsch–Gordan coefficient in equation (12), having at least one zero element, suggests that μ can be interpreted as a *helicity* quantum number. Physically this means that the chosen axis is the one corresponding to a zero component of the orbital angular momentum vector l and therefore lies in the plane of the orbit, like the Runge–Lenz vector [15, 17]; an operation of this kind finds its analogues in several contexts: we mention the *space-fixed* to *body-fixed* transformation in molecular collisions [33], the Hund's cases (*e*) → (*c*) transformation in molecular spectroscopy and atomic scattering [34, 35] and the passage between symmetric and asymmetric coordinates in the hyperspherical treatment of the three-body problem [36, 37].

The coefficient connecting the polar and Zeeman basis [3] was called Z:

$$\langle lm|\lambda m\rangle = (-)^{l+\lambda} Z^{nm}_{l\lambda}. \tag{13}$$

The overlap between spherical and Zeeman states, was originally derived as a sum of the product of two vector coupling coefficients [19] (see figure 1):

$$\begin{aligned} Z^{n,m}_{l,\lambda} = \sum_{\mu} (-)^{\alpha} & \left\langle \frac{n-1+m}{2}, -\frac{\mu}{2}; \frac{n-1-m}{2}, \frac{\mu}{2} \middle| l, 0 \right\rangle \\ \times & \left\langle \frac{n-1+m}{2}, -\frac{\mu}{2}; \frac{n-1-m}{2}, \frac{\mu}{2} \middle| \lambda, 0 \right\rangle \end{aligned} \tag{14}$$

where $\alpha = (n-1-m-\mu)/2 + l + \lambda$ is an integer. It is worth noticing that the $Z^{n,m}_{l,\lambda}$ coefficient is strictly related to $O(4)$-representation function. The phase $(-)^{-\mu/2}$ is equivalent to a rotation of the coordinate system through an angle $\pi/2$ in the four-dimensional space. If this phase were omitted, the sum would be $\delta_{l\lambda}$ [38].

By direct integration or by specializing overlap coefficients between alternative harmonics [38] we are able to write it directly as a single sum of the Racah type. This sum [39] is a hypergeometric function ${}_4F_3$ of unit argument:

$$\begin{aligned} Z^{n,m}_{l,\lambda} = \sqrt{(l+\tfrac{1}{2})(\lambda+\tfrac{1}{2})}[C(l)\cdot C(\lambda)]^{1/2} \cdot \frac{\Gamma\left(\dfrac{n-m-q(l)-q(\lambda)}{2}\right)}{\Gamma(m+1)\Gamma\left(\dfrac{m+n+1+q(l)+q(\lambda)}{2}\right)} \\ \times {}_4F_3\left(\begin{matrix} \dfrac{m-l+q(l)}{2}, \dfrac{m+l+q(l)+1}{2}, \dfrac{m-\lambda+q(\lambda)}{2}, \dfrac{m+\lambda+1+q(\lambda)}{2} \\ m+1, \dfrac{m-n+1+q(l)+q(\lambda)}{2}, \dfrac{m+n+1+q(l)+q(\lambda)}{2} \end{matrix}; 1\right) \end{aligned} \tag{15}$$

where

$$C(k) = \frac{\left(\dfrac{n+k-1}{2}+p(k)\right)!\left(\dfrac{k+m}{2}-q(k)\right)! \times \left(\dfrac{k-m}{2}-q(k)\right)!\Gamma\left(\dfrac{n-k}{2}+p(k)\right)}{\Gamma\left(\dfrac{n+k+2}{2}+p(k)\right)\Gamma\left(\dfrac{m+k+1}{2}+q(k)\right) \times\Gamma\left(\dfrac{k-m+1}{2}+q(k)\right)\left(\dfrac{n-k-1}{2}-p(k)\right)!}$$

and

$$p(k) = -\frac{1+(-1)^{k-n}}{4}, q(k) = \frac{(-1)^{k-m}-1}{4}$$

(see [3] for the explicit expression and table 1 for numerical values).

The sum in (15) can also be connected with Racah polynomials [38], although it cannot be reduced to the ordinary Racah or 6-*j* coefficient which performs angular momentum recoupling. Indeed, like a Racah recoupling coefficient $Z^{n,m}_{l,\lambda}$ enjoys orthonormal properties with respect to summation on two angular momentum quantum numbers (l and λ), but contains the projection quantum number m. We found that the Z coefficient can be compactly written as a *generalized* 6-*j* symbol [3,

Table 1. Non-zero $Z^{n,m}_{l,\lambda}$ matrix elements up to $n = 4$.

$nl\lambda m$	$Z^{n,m}_{l,\lambda}$	$nl\lambda m$	$Z^{n,m}_{l,\lambda}$
1000	1	4111	$\frac{1}{5}$
2100	1	4210	$\frac{2}{\sqrt{5}}$
$211-1$	-1	$422-1$	-1
2111	1	4221	1
3000	$\frac{1}{3}$	4300	$\frac{2}{\sqrt{5}}$
3110	1	$431-1$	$-\frac{2\sqrt{6}}{5}$
3200	$\frac{2\sqrt{2}}{3}$	4311	$\frac{2\sqrt{6}}{5}$
$321-1$	-1	$432-2$	1
3211	1	4320	$-\frac{1}{\sqrt{5}}$
$322-2$	1	4322	1
$322-1$	-1	$433-3$	-1
3220	$-\frac{1}{3}$	$433-1$	$\frac{1}{5}$
3222	1	4331	$-\frac{1}{5}$
4100	$\frac{1}{\sqrt{5}}$	4333	1
$411-1$	$-\frac{1}{5}$		

40] (care is needed when the standard 6-*j* symbols symmetries are considered, see [41]):

$$Z^{n,m}_{l,\lambda} = (-)^{(l+\lambda)/2+1+p(l)+p(\lambda)}\sqrt{(l+\tfrac{1}{2})(\lambda+\tfrac{1}{2})}\begin{Bmatrix} p(\lambda)-\frac{1}{4} & \frac{n-1}{2} & \frac{\lambda}{2}-\frac{1}{4} \\ p(l)-\frac{1}{4} & \frac{m-1}{2} & \frac{l}{2}-\frac{1}{4} \end{Bmatrix}. \qquad (16)$$

Note that $Z^{n,m}_{l,\lambda}$ *is zero when* $n+l+\lambda+m$ *is even* and shows the symmetries $Z^{n,m}_{l,\lambda} = Z^{n,-m}_{l,\lambda}$ and $Z^{n,m}_{l,\lambda} = Z^{n,m}_{\lambda,l}$. Moreover it enjoys most properties of ordinary 6-*j* symbols, such as several recurrence relationships [42], including a three-term one which allows accurate and efficient calculations [43–45] even for large values of the arguments.

3. Atomic and molecular structure and the breaking of hyperspherical symmetry

The generalization of Fock's treatment to spaces of higher mathematical dimensions than the physical one [4] allows us to study atomic and molecular structure from the point of view of the broken symmetry of hyperspheres. As a matter of fact the quantum mechanics of atoms and molecules can be discussed in terms of the breaking of the hyperspherical symmetry of a d-dimensional hydrogenoid atom—$d = 3(N-1)$ for N body Coulomb problems—due to the introduction of further charged particles (electrons and/or nuclei). Thus in configuration space, Sturmian basis functions [4] (multidimensional hydrogenic orbitals of fixed energy, see the following) can be used as expansion bases sets to build up atomic and molecular orbitals. Since the counterparts of d-dimensional Sturmian functions in momentum space are $(d+1)$-dimensional hyperspherical harmonics, the possibility of exploiting different parametrizations of the $(d+1)$-dimensional sphere can be considered. Additionally, one can choose among alternative hyperspherical harmonics pertaining to different subgroup chain reductions of the original $(d+1)$-dimensional rotation group and thus possessing different symmetry properties. The corresponding superposition coefficients can be written in terms of vector coupling or recoupling coefficients (and their extensions to include as arguments multiples of 1/4) and, due to the duality between configuration and momentum space, can also be used to connect alternative Sturmian bases in configuration space.

The method which we will discuss, from a formal viewpoint, is general and thus can be applied to any N-body Coulomb problem. In this section we analyse the three-body Coulomb problem, exploiting considerations on the symmetry of the seven-dimensional rotational group and involving a mapping on the S^6 hypersphere. The matrix elements which have to be calculated to set up the secular equation can be very compactly formulated. All integrals can be written in closed form as matrix elements corresponding to coupling, recoupling or transformation coefficients of hyperangular momenta algebra.

The results that we have obtained represent an exploration about the power of this formulation, with particular reference to convergence of alternative sets. This point of view is crucial to work out approximation and truncation techniques for the basis sets and to make this formulation not only formally complete, but also computationally efficient.

3.1. *Hyperspherical coordinate representation*

In the hyperspherical approach to the N-body problem (see [46] for an elementary account), the first step consists of separating the centre mass motion and then, after mass scaling the coordinates, one is led to the study of a single particle—with reduced mass $\mu = (\prod m_i / \sum m_i)^{1/(N-1)}$—in a d-dimensional space. In this space the position of the particle is defined by a vector $\mathbf{r}$ whose length is the hyperradius r

$$r^2 = \sum_{i=1}^{d} x_i^2 \tag{17}$$

where x_i are mass weighted Cartesian coordinates. The orientation of the vector $\mathbf{r}$ is specified by $d-1$ hyperangles, collectively denoted by ω, which span the surface of the hypersphere. The hyperangles ω can be chosen in a number of ways: any alternative angular parametrization, corresponding to alternative reduction schemes of the rotation group $O(d)$ into its subgroups, carries quantum numbers which appear as labels for the harmonics and are conveniently interpreted as eigenvalues of hyperangular momenta or their 'projections'. In the following it will be shown how the choice of the most suitable parametrization for the problem to be solved is crucial in this treatment.

The Schrödinger equation for a system of N particles interacting through Coulomb forces then can be written in the form (atomic units will be implied throughout):

$$\left[-\frac{1}{2}\left(\frac{1}{r^{d-1}}\frac{\partial}{\partial r}r^{d-1}\frac{\partial}{\partial r}-\frac{\Lambda^2}{r^2}\right)+V-E\right]\Psi(\mathbf{r})=0. \tag{18}$$

Λ^2 is the generalized angular momentum operator, whose eigenfunctions are hyperspherical harmonics, obeying the following relationship:

$$\Lambda^2 Y_{\lambda\sigma}(\omega)=-\lambda(\lambda+d-2)Y_{\lambda\sigma}(\omega) \tag{19}$$

where λ is the grand orbital angular momentum quantum number and σ collectively represents the set of $d-2$ *projections* of λ (i.e. the quantum numbers σ are eigenvalues of the rotation operators of the subgroups related to the chosen chain reduction).

The Coulomb potential in hyperspherical coordinates takes the simple factorized form [47, 48]:

$$V=-\frac{\Omega(\omega)}{r} \tag{20}$$

where $\Omega(\omega)$ plays the role of an anisotropic charge. Owing to this term equation (18) is not separable: if $\Omega(\omega)$ were a constant equation (18) would coincide with the Schrödinger equation of the multidimensional hydrogen atom, whose solutions can be obtained exactly [4] as d-dimensional Sturmian basis functions. (Features and properties of this orthonormal set can be found, for example, in [49, 50].) Therefore, in configuration space the many-body Coulomb problem is isomorphic to that of a multidimensional hydrogen atom with an anisotropic charge. For this reason we feel encouraged to use d-dimensional Sturmian basis sets to expand multielectronic orbitals $\Psi(\mathbf{r})$.

Furthermore, an attractive feature of the Sturmian basis—besides properties such as orthonormality, completeness, discretization of the continuum—is its direct relationship with the hyperspherical harmonics. This connection is revealed by the generalization of the Fock stereographic projection (section 2) to multidimensional space [4]: the d-dimensional momentum space, related by Fourier transform to the d-dimensional configuration space, is mapped onto a $(d+1)$-sphere of unit radius S^{d+1}, so that the integral Schrödinger equation for the hydrogen atom in momentum space becomes a Helmholtz type differential equation whose solutions, apart from a constant weight function, are $(d+1)$-dimensional hyperspherical harmonics, that is eigenfunctions of a multidimensional Laplace operator. The possibility of choosing among alternative hyperspherical harmonics, as already remarked, corresponds, in configuration space, to the possibility of dealing with different Sturmian basis sets (arising from the separation of the hydrogen atom Schrödinger equation in different sets of coordinates [4], see [2] for the physical case), which are connected by the superposition matrix elements identical to those involved by the hyperspherical harmonics. These matrix elements can be written and explicitly calculated as (generalized) vector coupling or recoupling coefficients, that is as elements of an angular momentum algebra that admits an extended set of quantum numbers.

3.2. *Sturmian basis sets as multielectronic atomic orbitals*

In configuration space the solution of equation (18) is expanded into a series of generalized d-dimensional Sturmian functions [4]:

$$\Psi(\mathbf{r})=\sum_{n\lambda\sigma}c_{n\lambda\sigma}u_{n\lambda\sigma}(\mathbf{r}) \tag{21}$$

where $u_{n\lambda\sigma}(\mathbf{r})$ can be expressed as the product between a radial and an angular part

$$u_{n\lambda\sigma}(\mathbf{r}) = u_{n\lambda}(r)\, Y_{\lambda\sigma}(\omega_{d-1}). \tag{22}$$

$Y_{\lambda\sigma}(\omega_{d-1})$ is a hyperspherical harmonic (see equation (19)) on the d-dimensional sphere and the radial function is

$$\begin{aligned} u_{n\lambda}(r) = (2p_0)^{d/2} & \frac{[(n-\lambda-1)!]^{1/2}}{[(2n+d-3)(n+\lambda+d-3)!^3]^{1/2}} (2p_0 r)^{\lambda} \\ & \times \exp(-p_0 r) L_{n-\lambda-1}^{2\lambda+d-2}(2p_0 r) \end{aligned} \tag{23}$$

where $L_{n-\lambda-1}^{2\lambda+d-2}(2p_0 r)$ is a Laguerre polynomial (see appendix of [2] for different notations used in the literature) and $p_0^2 = -2E$. The Coulomb Sturmian basis set is thus seen to be composed of exactly the same type of functions known as hydrogenic orbitals, for which the solution of the Schrödinger equation gives $p_0 = 2Z/(2n+d-3)$ (where Z is the nuclear charge). The latter set, however, is not complete unless one also includes the continuum states, which are very difficult to handle. Using the Sturmian sets as expansion bases leads to secular equations where no restriction is assumed between n and p_0 and when p_0 is obtained by diagonalization, energy is recovered as $p_0^2 = -2E$. Therefore, this approach is in the spirit of the very early work by Hylleraas and Slater, providing an automatic optimization of the 'exponent' of the radial orbitals [51].

The functions $u_{n\lambda\sigma}(\mathbf{r})$ satisfy the following orthogonality relationship:

$$\int u_{n'\lambda'\sigma'}^{*}(\mathbf{r}) \frac{1}{r} u_{n\lambda\sigma}(\mathbf{r})\, \mathrm{d}\mathbf{r} = \frac{2p_0}{2n+d-3} \delta_{nn'} \delta_{\lambda\lambda'} \delta_{\sigma\sigma'}. \tag{24}$$

When the solution of the Schrödinger equation for an atom or molecule is expressed as a linear combination of generalized Sturmian functions, the secular equation takes an extremely simple form, as illustrated in [1]. By substituting equation (21) into Schrödinger equation (18) and considering that when using Sturmian functions one has [1]:

$$\left(\frac{1}{r^{d-1}} \frac{\partial}{\partial r} r^{d-1} \frac{\partial}{\partial r} - \frac{\Lambda^2}{r^2} \right) u_{n\lambda\sigma}(\mathbf{r}) = \left[-\frac{p_0(2n+d-3)}{r} + p_0^2 \right] u_{n\lambda\sigma}(\mathbf{r}), \tag{25}$$

we obtain

$$\sum_{n,\lambda,\sigma} \left[\frac{2\Omega(\omega) - p_0(2n+d-3)}{r} + p_0^2 + 2E \right] c_{n\lambda\sigma} u_{n\lambda\sigma}(\mathbf{r}) = 0. \tag{26}$$

If we now multiply on the left by $u_{n'\lambda'\sigma'}^{*}(\mathbf{r})$ and integrate on the whole space we get

$$\sum_{n,\lambda,\sigma} \left[\int u_{n'\lambda'\sigma'}^{*}(\mathbf{r}) \frac{2\Omega(\omega) - p_0(2n+d-3)}{r} u_{n\lambda\sigma}(\mathbf{r})\, \mathrm{d}\mathbf{r} \right] c_{n\lambda\sigma} = 0 \tag{27}$$

and using the orthonormality condition for the d-dimensional Sturmian (24)

$$\int Y_{\lambda'\sigma'}(\omega) Y_{\lambda\sigma}(\omega)\, \mathrm{d}\omega \int u_{n'\lambda'}(2p_0 r) \frac{1}{r} u_{n\lambda}(2p_0 r)\, \mathrm{d}(2p_0 r) = \frac{2p_0}{2n+d-3} \delta_{nn'} \delta_{\lambda\lambda'} \delta_{\sigma\sigma'} \tag{28}$$

one obtains the algebraic system

$$\sum_{n,\lambda,\sigma} \left(p_0 A_{nn'\lambda\lambda'\sigma\sigma'} - p_0^2 \delta_{nn'} \delta_{\lambda\lambda'} \delta_{\sigma\sigma'} \right) c_{n\lambda\sigma} = 0 \tag{29}$$

where

$$A_{nn'\lambda\lambda'\sigma\sigma'} = R_{nn'\lambda\lambda'}\Omega_{\lambda\lambda'\sigma\sigma'}. \tag{30}$$

Neglecting the uninteresting case $p_0 = 0$ one can rewrite equation (29) as a secular equation

$$[\mathbf{A} - p_0\mathbf{I}]\mathbf{c} = 0 \tag{31}$$

where $\mathbf{I}$ is the unit matrix. (The momentum space perspective will be shown to indicate that the factorization (30) of $\mathbf{A}$ into a radial and angular contribution can profitably be avoided. This can be crucial when λ is suspected not to be a 'good' quantum number.)

Previous derivations [1] (for three-body problem see [13]) can be consulted for details. Note, however, that the configuration space perspective provides no link between n and λ: here, $\lambda \leq n - 1$. The solution of the secular problem provides the coefficients $c_{n\lambda\sigma}$ as eigenvectors for the expansion of multielectronic orbitals and the eigenvalues p_0. In this case the eigenvalues of the secular equation (29) do not give directly the binding energy of the system in various states, but the latter can be obtained from the equation $p_0^2 = -2E$. The basic ingredients to solve equation (29) are the integral over the ω angular variables

$$\Omega_{\lambda\lambda'\sigma\sigma'} = \int Y^*_{\lambda'\sigma'}(\omega)\Omega(\omega)\, Y_{\lambda\sigma}(\omega)\,\mathrm{d}\omega \tag{32}$$

and the radial integral [36]

$$R_{nn'\lambda\lambda'} = 2\sqrt{\frac{(n'-\lambda'-1)!(n-\lambda-1)!}{(2n+d-3)(2n'+d-3)[(n'+\lambda'+d-3)!(n+\lambda+d-3)!]^3}}$$
$$\times \int \exp{(2p_0r)}(2p_0r)^{\lambda+\lambda'+d-2}L^{2\lambda'+d-2}_{n'-\lambda'-1}(2p_0r)L^{2\lambda+d-2}_{n-\lambda-1}(2p_0r)\,\mathrm{d}(2p_0r). \tag{33}$$

The result of the integration (32) will obviously depend on the selected parametrization for the angular variables and on the particular Coulomb system under analysis. As will be shown in the following, it can be expressed in terms of vector coupling and recoupling coefficients of (hyper)angular momenta. This result can be easily predicted since equation (32) is an integral on hyperspherical harmonics.

From the configuration space perspective the fact that also the explicit expression of the radial integral $R_{nn'\lambda\lambda'}$ depends only on the number of particles (i.e. on the dimension of configuration space) and not on the nature of the particles and that it can be written as a linear combination of vector coupling coefficients (as will be shown in the next section) might be surprising. However, this apparently unexpected result is explained by the underlying duality between multidimensional Coulomb Sturmians in configuration space and hyperspherical harmonics in momentum space: the analogue of integral (33) in reciprocal space would be an integral between hyperspherical harmonics. Thus the momentum space perspective allows the close relationship between the angular integral $\Omega_{\lambda\lambda'\sigma\sigma'}$ and $R_{nn'\lambda\lambda'}$ to be realized and the quantum number n emerges as a label of hyperspherical harmonics.

3.3. *The three-body problem*

We now turn to the application of the hyperspherical method to the problem of three particles interacting through Coulomb forces. Our main focus is on bielectronic systems (helium and its isoelectronic series) where two of the particles are identical, while the mass of the other one is much heavier. However, this approach is completely general and can be immediately extended to whatsoever mass ratios. In section 4.1 a comparison is reported between numerical results for the bielectronic series and systems with different mass ratios: H_2^+ beyond a fixed nuclei scheme and $e^-e^+e^-$. In hyperspherical coordinates, the Schrödinger equation for the three-body problem can be written according to equation (18):

$$\left[-\frac{1}{2}\left(\frac{1}{r^5}\frac{\partial}{\partial r}r^5\frac{\partial}{\partial r}-\frac{\Lambda^2}{r^2}\right)+V-E\right]\Psi(\mathbf{r})=0. \tag{34}$$

This equation differs in the various systems only for the potential expression V. If r_{12}, r_{13} and r_{23} are the distances between the particles, the Coulomb potential can be written as

$$V=\frac{z_1z_2}{r_{12}}+\frac{z_1z_3}{r_{13}}+\frac{z_2z_3}{r_{23}} \tag{35}$$

where z_1, z_2 and z_3 are their charges. In the hyperspherical parametrizations, three mass factors c_1, c_2 and c_3 [13, 52] appear (see (45) and (53) below):

$$c_1=\sqrt{2}b\sin\delta_1;\qquad c_2=\sqrt{2}b\sin\delta_2;\qquad c_3=\sqrt{2}/b \tag{36}$$

with

$$b^2=\frac{m_1+m_2}{m_1m_2}\times\sqrt{\frac{m_1m_2m_3}{m_1+m_2+m_3}}.$$

The phase angles δ_i are related to the particle masses by

$$\begin{aligned}\tan\delta_1&=\frac{1}{b^2}\left(\frac{m_1+m_2}{m_1}\right)\\ \tan\delta_2&=-\frac{1}{b^2}\left(\frac{m_1+m_2}{m_2}\right).\end{aligned} \tag{37}$$

For systems with two identical particles we have $c_1=c_2\equiv c$ and $\delta_1=\pi-\delta_2\equiv\delta$. The corresponding values of these parameters for some systems are listed in table 2 [13].

The value of parameters c, c_3 and δ for the helium isoelectronic series remains substantially the same, as the nucleus for these systems can be considered infinitely heavier than the electrons, in particular as the atomic number increases (even if in our method this approximation is not required). Thus the Coulomb potential given by equation (35) for each term of the series differs only for the charge z_3.

Appropriately to a six-dimensional configuration space, six-dimensional Sturmian functions will have to be used, whose radial part $u_{n\lambda}(2p_0r)$ is

$$u_{n\lambda}(2p_0r)=\left[\frac{(2p_0)^6(n-\lambda-1)!}{(2n+3)[(n+\lambda+3)!]^3}\right]^{1/2}\mathrm{e}^{-p_0r}(2p_0r)^\lambda L_{n-\lambda-1}^{2\lambda+4}(2p_0r) \tag{38}$$

obtained by equation (23) setting $d=6$.

The explicit expression of radial integrals can now be worked out with the help of the equation on page 785 of [53] to give

Table 2. Values of parameters used in equation (36).

	c	c_3	δ
$H^-, He, Li^+, \dots, O^{6+}$	$\sqrt{2}$	1	$\frac{\pi}{4}$
H_2^+	$\sqrt{2}$	42.85	0.016498
$e^-e^+e^-$	1	1	$\frac{\pi}{6}$

$$R_{nn'\lambda\lambda'} = 2(-)^{n-\lambda-2+n'-\lambda'} \cdot \left[\frac{(n'-\lambda'-1)!(n-\lambda-1)!}{(2n'+3)(2n+3)(n'+\lambda'+3)!(n+\lambda+3)!}\right]^{1/2}$$
$$\times \sum_k \frac{\Gamma(\lambda-\lambda'+1)\Gamma(\lambda'-\lambda+1)\Gamma(\lambda+\lambda'+k+5)}{k!(n-\lambda-k)!(n'-\lambda'-k)!\Gamma(k-n+\lambda'+1)\Gamma(k-n'+\lambda+1)} \qquad (39)$$

where the running index k can take all the integer values larger than the largest between $(n-\lambda'-1)$ and $(n'-\lambda-1)$ and smaller than the smallest between $n-\lambda$ and $n'-\lambda'$; in the other cases the integral vanishes. Note that equation (39) has to be compared with the radial integral of [13] (the n there corresponds to our $n-\lambda-1$), however the phase and the factor $[(n'-\lambda'-1)(n-\lambda-1)]^{1/2}$ are missing.

As we anticipated in the previous section $R_{nn'\lambda\lambda'}$ can also be expressed as a linear combination of vector coupling coefficients [39]:

$$R_{nn'\lambda\lambda'} = \frac{1}{(n'+\lambda+4)^{1/2}}\left[(n+\lambda+4)^{1/2}F + (n-\lambda-1)^{1/2}B\right] \qquad (40)$$

with

$$F = \left\langle \frac{2\lambda'+3}{2}, \frac{n'-\lambda-2}{2}, \frac{2\lambda+5}{2}, \frac{2n-n'-\lambda-2}{2} \middle| \frac{n'+\lambda+3}{2}, \frac{2n-n'+\lambda+3}{2} \right\rangle$$

$$B = \left\langle \frac{2\lambda'+3}{2}, \frac{n'-\lambda-2}{2}, \frac{2\lambda+5}{2}, \frac{2n-n'-\lambda}{2} \middle| \frac{n'+\lambda+3}{2}, \frac{2n-n'+\lambda+5}{2} \right\rangle$$

where F and B are Clebsch–Gordan coefficients, so $R_{nn'\lambda\lambda'}$ for a three-body Coulomb problem depends on the involved quantum numbers only and not on the nature of the system just like the angular integral. If we look at the problem from the momentum space point of view (see also figure 3(*a*)) the whole matrix $A_{nn'\lambda\lambda'\sigma\sigma'}$ can be in fact obtained from the integration over angular variables only, parametrizing the S^6 hypersphere embedded in a seven-dimensional Euclidean space. Thus the quantum numbers n and λ label the eigenvalues of the rotation operators of the seven-dimensional hypersphere S^6 and of a six-dimensional subspace respectively. Under this perspective the possibility of exploiting different parametrizations of S^6 whose symmetry properties are closer to those of the system represents an extremely attractive feature. This is important for example to eliminate the quantum number λ which, as will be shown in the following, is often a not too 'good' quantum number for many systems under investigation. Note that this possibility emerges only when considering the seven-dimensional hypersphere, that is in a momentum space perspective.

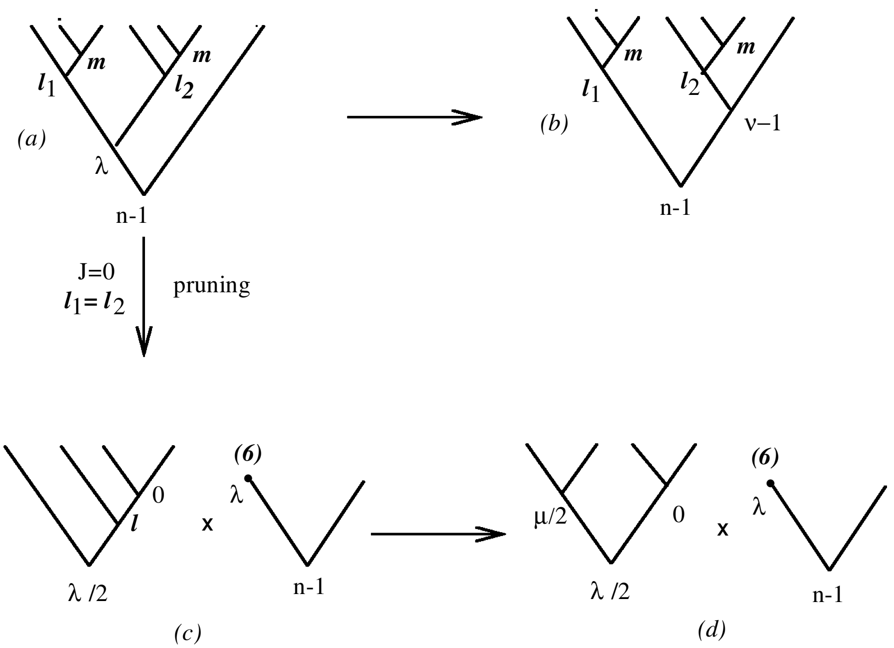


Figure 3. Hyperspherical harmonics for the three-body Coulomb problem in $d = 7$ momentum space by the tree graphical technique. Tree (*a*) represents a parametrization of the S^6 sphere, corresponding in terms of group theory to the following subgroup reduction chain: $O(7) \supset O(6) \supset O(3) \times O(3)$. Tree (*b*), obtained from tree (*a*) by *timber* vector coupling, involves a $O(7) \supset O(4) \times O(3)$ subgroup chain, where $O(4)$ is the parametrization in asymmetric coordinates for the physical hydrogen atom. The simplification of the symmetric harmonic (*a*) (see equation (46)) leads to a reduction of the dimensionality of the problem (tree (*c*)) and to the appearance of the $O(7) \supset O(4) \times O(3)$ subgroup reduction chain. By application of the timber coefficient (57) tree (*c*) leads to tree (*d*).

$R_{nn'\lambda\lambda'}$ vanishes for particular values of the quantum numbers n, n', λ, λ' [1]. This is the case for $\lambda = \lambda'$ when $n \neq n'$, for $\lambda > \lambda'$ when $n \leq n'$ and, since the matrix $\mathbf{R}$ is symmetric, for $\lambda < \lambda'$ when $n' \leq n$. When the element $R_{nn'\lambda\lambda'}$ vanishes the corresponding matrix element $A_{nn'\lambda\lambda'\sigma\sigma'}$ becomes zero, and the matrix to be diagonalized takes the structure of figure 4, with blank spaces representing zero elements. Angular parametrizations appropriate to describe states of definite total angular momentum will be discussed in the following sections.

3.4. *Asymmetric hyperangular parametrization*

Let us now turn to the question of the evaluation of matrix elements $\Omega_{\lambda\lambda'\sigma\sigma'}$. Our analysis starts from the following six-dimensional hyperspherical harmonics:

$$Y_{\lambda,l_1,l_2,m_1,m_2}(\chi,\theta_1,\theta_2,\phi_1,\phi_2) = N_{\lambda,l_1,l_2}\sin^{l_1}\chi\cos^{l_2}\chi P^{l_2+1/2,l_1+1/2}_{(\lambda-l_1-l_2)/2}(\cos 2\chi)\,Y_{l_1,m_1}(\theta_1,\phi_1)\,Y_{l_2,m_2}(\theta_2,\phi_2) \qquad (41)$$

where $Y_{l_1,m_1}(\theta_1,\phi_1)$ and $Y_{l_2,m_2}(\theta_2,\phi_2)$ are spherical harmonics, $P^{l_2+1/2,l_1+1/2}_{(\lambda-l_1-l_2)/2}(\cos 2\chi)$ is a Jacobi polynomial and N_{λ,l_1,l_2} is a normalization factor:

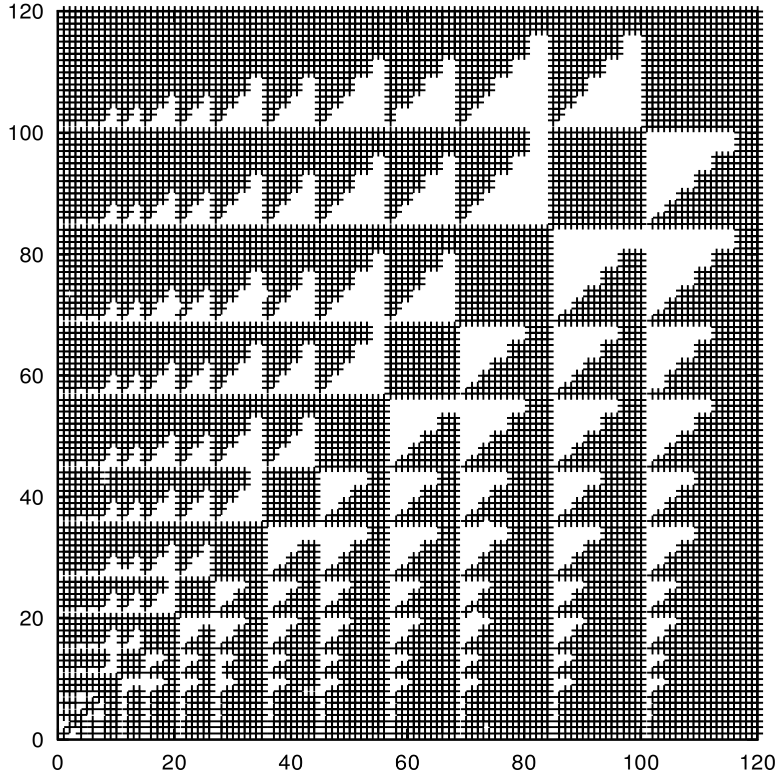


Figure 4. Structure of the matrix $A_{nn'\lambda\lambda'\sigma\sigma'}$ (equation (11)): non-zero elements are indicated with crosses. When the radial integral $I_{nn'\lambda\lambda'}$ is zero, the corresponding matrix element vanishes. The figure refers to the 120 × 120 matrix obtained by truncation on the quantum number n to $n = 15$ in the expansion of equation (21).

$$N_{\lambda,l_1,l_2} = \left\{ \frac{(2\lambda + 4)[(\lambda - l_1 - l_2)/2]!}{\Gamma[(\lambda + l_1 - l_2 + 3)/2]} \times \frac{\Gamma[(\lambda + l_1 + l_2 + 4)/2]}{\Gamma[(\lambda + l_2 - l_1 + 3)/2)]} \right\}^{1/2}. \tag{42}$$

This choice is motivated by the physical meaning of the quantum numbers labelling the harmonic (for H_2^+ l_1 represents the rotational angular momentum, l_2 the orbital angular momentum of the electron), m' and m'' are their projections onto the quantization axis and λ is the grand orbital momentum quantum number.

In order to obtain basis functions which are eigenfunctions of the total angular momentum J and of its projection M_J the harmonics in (41) have to be appropriately combined:

$$\begin{aligned} Y^{J,M_J}_{\lambda l_1 l_2} &= N_{\lambda,l_1,l_2} \sin^{l_1}\chi \cos^{l_2}\chi P^{l_2+1/2,l_1+1/2}_{(\lambda-l_1-l_2)/2}(\cos 2\chi) \\ &\quad \times \sum_{m_1 m_2} \langle l_1, m_1, l_2, m_2 | J, M_J \rangle Y_{l_1,m_1}(\theta_1, \phi_1) Y_{l_2,m_2}(\theta_2, \phi_2) \end{aligned} \tag{43}$$

where $\langle l_1, m_1, l_2, m_2 | J, M_J \rangle$ is a vector coupling coefficient.

Our next step will be the determination of $\Omega(\omega)$ according to this parametrization. The anisotropic charge contains all the information about the Coulomb interaction, depending on the mass, on the charge and on the distances of three particles, which can be defined as follows [52]:

$$\begin{aligned} r_{13} &= \frac{r}{b}\sqrt{\frac{1}{2}\left[1+\frac{m_3}{m}\right]}(1+\cos 2\delta\cos 2\chi-\sin 2\delta\sin 2\chi\cos\theta)^{1/2} \\ r_{23} &= \frac{r}{b}\sqrt{\frac{1}{2}\left[1+\frac{m_3}{m}\right]}(1+\cos 2\delta\cos 2\chi+\sin 2\delta\sin 2\chi\cos\theta)^{1/2} \\ r_{12} &= \frac{br}{\sqrt{2}}(1+\cos 2\chi)^{1/2} \end{aligned} \qquad (44)$$

where $\cos\theta=\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2)$.

The anisotropic charge $\Omega(\omega)$, which depends only on the internal angles χ and θ, then becomes

$$\begin{aligned} \Omega(\chi,\theta) = &\frac{z_1 z_3 c}{(1+\cos 2\delta\cos 2\chi-\sin 2\delta\sin 2\chi\cos\theta)^{1/2}} \\ &+\frac{z_2 z_3 c}{(1+\cos 2\delta\cos 2\chi+\sin 2\delta\sin 2\chi\cos\theta)^{1/2}}+\frac{z_1 z_2 c_3}{(1+\cos 2\chi)^{1/2}}. \end{aligned} \qquad (45)$$

In the following we will turn our attention to states of zero angular momentum, that is to S states for the helium and other bielectronic systems.

In this case, the dimensionality of the problem can be simplified [24]; the six-dimensional harmonics of equation (43), as illustrated in figure 3(c) can be reduced to a four-dimensional harmonics $Y_{\lambda/2}, l, 0(2\chi,\theta,0)$:

$$Y_{\lambda/2,l,0}(2\chi,\theta,0)=A_{\lambda/2,l}\sin^l 2\chi C^{l+1}_{\lambda/2-l}(\cos 2\chi)Y_{l,0}(\theta,0) \qquad (46)$$

where $C^{l+1}_{\lambda/2-l}(\cos 2\chi)$ is a Gegenbauer polynomial, $Y_{l,0}(\theta,0)$ a spherical harmonic and $A_{\lambda/2,l}$ the normalization factor:

$$A_{\lambda/2,l}=\frac{\Gamma(\lambda+l+3)}{2^{l+1}\Gamma\left(\frac{\lambda}{2}+3\right)}\left[\frac{(\lambda+2)\left(\frac{\lambda}{2}-l\right)!}{\Gamma\left(\frac{\lambda}{2}+l+2\right)}\right]. \qquad (47)$$

Note that the quantum number $\lambda/2$ has to be an integer, thus λ is even and $0\le l\le\lambda/2$, furthermore only even values of l are allowed [54].

Equation (32) can now be written as

$$\Omega_{\lambda\lambda' ll'}=\int Y_{\lambda/2,l,0}(2\chi,\theta,0)\Omega(\chi,\theta)Y_{\lambda'/2,l',0}(2\chi,\theta,0)\,\mathrm{d}\cos 2\chi\,\mathrm{d}\cos\theta. \qquad (48)$$

We now expand the anisotropic charge $\Omega(\chi,\theta)$ in terms of four-dimensional harmonics [48, 54, 55] (alternative approaches to calculate the $\Omega_{\lambda\lambda' ll'}$ matrix elements can be found in [56–58]):

$$\Omega(\chi,\theta) = \sqrt{\pi}\sum_{\lambda}\frac{1}{(\lambda+1)(\lambda+3)} \times \left[\frac{(\lambda+2)c_3}{\pi}Y_{\lambda/2+1,l,0}(2\chi,\theta,0) - 2^{3/2}c\sum_{l}Y_{\lambda/2+1,l,0}(2\delta,0,0)\,Y_{\lambda/2+1,l,0}(2\chi,0,0)\right]. \tag{49}$$

Substituting (49) into (48) yields [55]

$$\Omega_{\lambda\lambda',ll'} = 16\sqrt{2}\pi\sum_{\bar{\lambda}\bar{l}}\frac{1}{(\bar{\lambda}+1)(\bar{\lambda}+3)}\left[\frac{c_3\left(\frac{\bar{\lambda}}{2}+1\right)}{\sqrt{2\pi^2}} - cY_{\bar{\lambda}/2+1,\bar{l},0}(2\delta,0,0)\right] \times \left[\frac{(2l+1)(2l'+1)\left(\frac{\lambda}{2}+1\right)\left(\frac{\lambda'}{2}+1\right)}{2\pi^2}\right]^{1/2}\langle l',0,l,0;\bar{l},0\rangle \times \begin{Bmatrix} \frac{\lambda'}{4} & \frac{\lambda}{4} & \frac{\bar{\lambda}}{4} \\ \frac{\lambda'}{4} & \frac{\lambda}{4} & \frac{\bar{\lambda}}{4} \\ l' & l & \bar{l} \end{Bmatrix} \tag{50}$$

where

$$\bar{\lambda} = |\lambda'-\lambda|, |\lambda'-\lambda|+4,\ldots,\lambda'+\lambda-4,\lambda'+\lambda;$$

$$\bar{l} = |l'-l|, |l'-l|+2,\ldots,l'+l-2,l'+l.$$

Equations (40) and (50) can now be inserted into the secular equation (29), whose solution, as will be shown in the following, gives the energy spectrum.

A drastic simplification of equation (50) can be obtained considering states where the quantum number l is zero:

$$\Omega_{\lambda\lambda',00} = \frac{16}{\sqrt{2\pi^2}}\sum_{\bar{\lambda}}\frac{\left(\frac{\bar{\lambda}}{2}+1\right)c_3 - cC^{1}_{\bar{\lambda}/2}(\cos(2\delta+\pi))}{(\bar{\lambda}+1)(\bar{\lambda}+3)} \tag{51}$$

where $C^1_{\lambda}(x)$ is a special Gegenbauer polynomial, which can be calculated by recursion relations ([59, p. 1030]).

This expression can be very useful when it is sufficient to consider states with $l = 0$, that is when the quantum number l is a 'good' quantum number (this is the case for H_2^+, as will be shown in the following).

3.5. *Symmetric hyperangular parametrization*

As mentioned before, when $J = 0$ the motion of three particles evolves on a four-dimensional S^3 hemisphere. Alternative angular parametrizations can be built for S^3 [15]; among those, besides the parametrization previously examined, we can choose angular variables corresponding to the 'symmetric parametrization' [60], which was initially proposed by Smith. In this representation the four-dimensional hyperspherical harmonics can be expressed in terms of Wigner functions $D^{\lambda/4}_{\mu/4,\mu/4}(2\Phi, 4\Theta, 0)$:

$$Y_{\lambda/2,0,\mu/2}(2\Theta, 0, 2\Phi) = (-)^{\mu/2}\left(\frac{\lambda/2+1}{2\pi^2}\right)^{1/2} \times D^{\lambda/4}_{\mu/4,\mu/4}(2\Phi, 4\Theta, 0) \tag{52}$$

and $\Omega(\omega)$ now takes the following form:

$$\Omega(\Theta, \Phi) = \frac{z_3 z_2 c}{\sqrt{1+\cos 2\Theta \cos 2(\Phi+2\delta)}} + \frac{z_1 z_3 c}{\sqrt{1+\cos 2\Theta \cos 2(\Phi-2\delta)}} + \frac{z_2 z_1 c_3}{\sqrt{1+\cos 2\Theta \cos 2\Phi}}. \tag{53}$$

The integral (32) becomes

$$\Omega_{\lambda\lambda'\mu\mu'} = \int D^{\lambda/4}_{\mu/4,\mu/4}(2\Phi, 4\Theta, 0)\Omega(\Theta, \Phi) D^{\lambda'/4}_{\mu'/4,\mu'/4}(2\Phi, 4\Theta, 0)\, \mathrm{d}\cos 4\Theta\, \mathrm{d}\cos 2\Phi \tag{54}$$

and can be solved by expanding $\Omega(\Theta, \Phi)$ in terms of Wigner functions [13, 47]

$$\Omega(\Theta, \Phi) = 16(2\pi)^{1/2} \sum_{\lambda,\mu} \frac{[(\lambda+2)(2-\delta_{\mu 0})]^{1/2}}{(\lambda+1)(\lambda+3)} (c_3 - c\cos 2\delta\mu) D^{\lambda/4}_{\mu/4,\mu/4}(2\Phi, 4\Theta, 0). \tag{55}$$

Once more the evaluation of the matrix elements $\Omega_{\lambda\lambda'\mu\mu'}$ reduces to an integration of the product of three hyperspherical harmonics.

Inserting expansion (55) in (54) yields

$$\Omega_{\lambda\lambda'\mu\mu'} = \frac{8\sqrt{2}}{\pi}\left[\left(\frac{\lambda}{2}+1\right)\left(\frac{\lambda'}{2}+1\right)\right]^{1/2} \cdot \sum_{\alpha} \frac{(-1)^{\alpha}}{(2\alpha+1)(2\alpha+3)} \times \left([c\cos\delta(\mu+\mu') - (-)^{(\mu+\mu')/2} c_3] \left\langle \frac{\lambda}{4}, \frac{\mu}{4}, \frac{\lambda'}{4}, \frac{\mu'}{4} \middle| \frac{\alpha}{4}, \frac{\mu+\mu'}{4} \right\rangle^2 + [c\cos\delta(\mu-\mu') - (-)^{(\mu-\mu')/2} c_3] \left\langle \frac{\lambda}{4}, \frac{\mu}{4}, \frac{\lambda'}{4}, -\frac{\mu'}{4} \middle| \frac{\alpha}{4}, \frac{\mu-\mu'}{4} \right\rangle^2 \right) \tag{56}$$

which turns out to be extremely useful for numerical evaluation: recurrence relationships for the Clebsch–Gordan coefficients [6, 45] can be exploited to calculate the Ω matrix elements with an extremely high accuracy and effectiveness. The quantum number μ has the following range $0 \le \mu \le \lambda$ and $\mu/2$ must have the same parity as $\lambda/2$, i.e. it changes as $\mu = \lambda, \lambda - 4, \ldots, 0$ (or 2 according to parity).

It is worth noting that the hyperspherical harmonics of equations (52) and (46) are connected by the orthogonal transformation [24] (see figure 3(*d*)):

$$\sum_{l} (-)^{(\lambda-\mu)/4} (\imath)^{l} \left\langle \frac{\lambda}{4}, -\frac{\mu}{4}; \frac{\lambda}{4}, \frac{\mu}{4} \middle| l0 \right\rangle Y_{\lambda/2,l,0}(2\chi, \theta, 0) = \left(\frac{\lambda/2+1}{2\pi^2}\right)^{1/2} D^{\lambda/4}_{\mu/4,\mu,4}(2\Phi, 4\Theta, 0). \tag{57}$$

Therefore, the elements of equation (50), numerically more complicated because of the presence of $9j$ coefficients, can also be obtained by means of the above orthogonal transformation.

3.6. *Alternative parametrizations*

A typical feature of the Sturmian basis sets is their relationship with hyperspherical harmonics belonging to a space of a dimension higher by one. As shown in [4, 40], the different harmonics corresponding to alternative parametrizations of the hypersphere can be connected by vector coupling and recoupling coefficients (and their extensions to include multiples of 1/4 as arguments [41]). The orthonormal transformations that connect harmonics in momentum space are identical to those connecting the corresponding eigenfunctions in configuration space, because of the reciprocity between the two spaces. Thus one can exploit the overlap (coupling and recoupling coefficients) between their counterparts (hyperspherical harmonics) in momentum space, in order to introduce alternative basis sets in configuration space (with no need of the explicit expression for the corresponding eigenfunctions).

The search for alternative bases, labelled by different quantum numbers, is extremely important: reduced basis sets, with better convergence properties, can be obtained by considering truncations on specific quantum numbers. Since the above complete sets show a slow convergence (see next section), this feature is not negligible. For example the quantum number λ, as will be shown in section 4, is not a suitable quantum number for most of the three-body problems which we have analysed, evidently because it cannot be put in any correspondence to any physical feature of the system. For this reason in the following we will propose the introduction of an alternative quantum number which could efficiently substitute λ from the viewpoint of convergence of the expansion.

The Fourier transform of the six-dimensional Sturmian function in the asymmetric hyperspherical parametrization (see section 3.4) is a seven-dimensional hyperspherical harmonic [4] acting on S^6, which corresponds in terms of group theory to the following reduction of the $O(7)$ rotational group into its subgroups: $O(7) \supset O(6) \supset O(3) \times O(3)$. In this sense the quantum number n, which is the quantum number of a seven-dimensional angular momentum, can be defined as *grand principal quantum number* [22].

Alternative subgroup chain reductions can be obtained exploiting the appropriate overlap between the seven-dimensional harmonics involved; among those the reduction $O(7) \supset O(4) \times O(3)$ leads to the elimination of λ and the introduction of a quantum number—which can be denoted by ν in analogy with the principal quantum number n of the hydrogen atom in the physical case—corresponding to the angular momentum on a four-dimensional sphere S^3. The different $O(7)$ parametrizations and the corresponding hyperspherical harmonics involved are shown in figures 3(a) and (b) by the tree method, together with their simplification when $J = 0$. The superposition (or timber coefficient [61]) between the two harmonics can be written as a Racah polynomial [38, 39, 41], that is as a hypergeometric sum of ${}_4F_3(1)$ type, and can be written as an extended 6-j symbol, whose explicit expression when $l_1 = l_2 = l$ is

$$T^{n,l}_{\nu-1,\lambda} = (-)^{(\nu+\lambda-l-2-p)/2}[\nu(\lambda+2)]^{1/2}\begin{Bmatrix} -\frac{1}{4}-\frac{p}{2} & \frac{\lambda+1}{2} & \frac{n}{2}+\frac{1}{4} \\ -\frac{l}{2}-\frac{3}{4} & \frac{\nu-1}{2} & \frac{l}{2}-\frac{1}{4} \end{Bmatrix} \tag{58}$$

where $p = 0$ when $\nu - 1$ is even or $p = 1$ when $\nu - 1$ is odd. The application of this coefficient to the matrix elements of the secular equation leads to an energy spectrum where the states are labelled with n, ν, l. The quantum number ν must have the same parity of $n - l - 1$; because of the parity restrictions on l this results in ν being even when $n - 1$ is even and odd when $n - 1$ is odd. Numerical results on the behaviour of this kind of basis set will be given in the following section.

4. Applications

In section 4.1 numerical results will be presented to test the effectiveness in terms of convergence properties for alternative parametrizations and truncations of the basis sets. Section 4.2 is an account of progress in numerical approaches, approximations, generalizations and extensions.

4.1. *Benchmark numerical results*

The secular equation (29) is completely general and thus can be applied to any three-body Coulomb problem: only the numerical values of parameters c, c_3 and δ (see table 2), which depend on the mass of the particles, and the values of charges (z_1, z_2, z_3) vary. For helium and the other bielectronic systems, for which $m_1 = m_2 \ll m_3$, the parameter c_3 is practically the same, so the only parameter which effectively varies along the series is the nuclear charge z_3. Therefore, the performances of the different bases employed in the explicit construction of the matrix elements will be discussed as a function of z_3. These results will then be compared with those obtained for two other benchmark systems where the parameters c, c_3 and δ also vary: H_2^+ beyond the Born–Oppenheimer approximation $(m_1 = m_2 \gg m_3)$ and $e^-e^+e^-$ $(m_1 = m_2 = m_3)$.

The matrix arising from the solution of secular equation (29) is symmetric, in principle infinite, and, after proper truncation, can be diagonalized by standard techniques. Table 3 reports the ground state energy values for some different three-body problems in a 'closed shell' representation, that is by truncation on the quantum number n, considering all the allowed states in the shell. Such a truncation scheme clearly leads to identical results for all the different basis sets. This kind of set shows a slow convergence; for bielectronic systems the convergence, especially for the first terms of the series, improves as the charge value increases, as can be seen from figure 5 where the per cent deviation on the ground state energy is reported as a function of the nuclear charge. When the value of z_3 increases, the third term of the right-hand side in equation (45), which is constant as z_3 varies and takes into account the electron–electron interaction, becomes more and more negligible compared to the nucleus–electron interaction, which is proportional to z_3. For H_2^+ the convergence is particularly slow. Comparison with the best available values for the ground state energies is also illustrated, although only few significant figures are reported. For example the best variational ground state energy of He is $-2.903\,724\,377\,034\,119\,5$ au [67], while for $e^-e^+e^-$ it is $-0.262\,005\,070\,232$ au [68].

It is worth noting that in table 3 we reported the eigenvalue p_0 rather than the energy; in fact from equation (29) p_0 is obtained and then, from $p_0^2 = -2E$, the

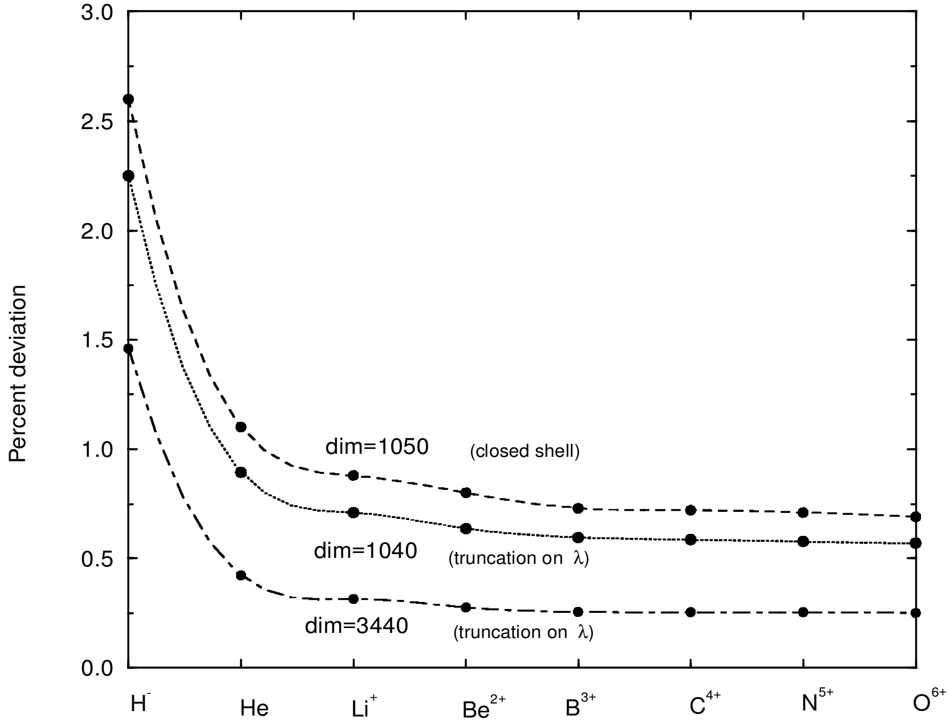


Figure 5. Per cent deviation from exact values for the ground state energy of the helium isoelectronic series. The dashed line is obtained by a 'closed shell' approximation (section 4.1), truncating on $n = 20$ on the expansion (21), while the dotted line corresponds to a truncation on $\lambda = 22$ and considering n up to 40: this leads to a set of slightly less dimensions and shows that the convergence improves by appropriately cutting on λ. This is also illustrated by the dashed–dotted line which represents the convergence of an expansion of larger dimension, obtained for $n = 100$ by truncation at $\lambda = 22$.

energy E can be calculated. As a consequence the energy at first seems to increase (corresponding to negative values of p_0) and then begins to decrease (for $p_0 > 0$). For this reason Whitten and Sims in their pioneering work [13] were led to the erroneous pessimistic conclusion that for H_2^+ the method was not variationally converging. Indeed it is important to remark that when solving secular equations by this technique, the variational theorem is satisfied, provided that the convergence is considered on p_0, rather than on E. This follows from the completeness of the basis set. By truncating also on λ and including for any fixed λ all the allowed values of μ or l in the symmetric or asymmetric representation, respectively, the convergence improves rapidly for the bielectronic series, as can be seen in table 4: once again this is especially remarkable for the first terms of the series. This behaviour is shown in figure 5 where the convergence of a λ truncated set is illustrated by comparison with that of a closed shell basis set of similar dimensions.

The most suitable value for truncation on λ depends on the particular system and on the number of states with different n in expansion (21). For the bielectronic series we found out that this value is around $\lambda = 24$ for $n_{\max} \approx 100$. Note that in [69], using an adiabatic approach with non-adiabatic perturbation corrections, a value of

Table 3. Ground state energy E and maximum n values and overall dimension (dim.) of the **A** matrix for bielectronic systems for 'closed-shell' truncation schemes.

H^-			He			Be^{2+}			O^{6+}			H_2^+			$e^-e^+e^-$		
dim.	n_{max}	E (au)	dim.	n_{max}	E (au)	dim.	n_{max}	E (au)	dim.	n_{max}	E (au)	dim.	n_{max}	p_0 (au)	dim.	n_{max}	E (au)
250	20	−0.5031	250	20	−2.8423	250	20	−13.444	250	20	−58.36	250	20	−0.6005	140	16	−0.2317
504	26	−0.5090	1050	34	−2.8720	504	26	−13.503	504	26	−58.59	1140	35	0.1926	1430	38	−0.2543
1050	34	−0.5139	1892	42	−2.8796	1050	34	−13.548	1050	34	−58.76	3094	50	0.5177	2756	48	−0.2562
exact [62]		−0.52775	exact [63]		−2.9037	exact [64]		−13.656	exact [65]		−59.17	exact [66]		1.0926	exact [62]		−0.2620

Table 4. Ground state energy E and maximum λ and corresponding dimension (dim.) of the **A** matrix for bielectronic systems by truncation scheme on λ (the range of μ is complete at each λ).

H^-				He				B^{3+}				O^{6+}			
dim.	n_{max}	λ_{max}	E (au)	dim.	n_{max}	λ_{max}	E (au)	dim.	n_{max}	λ_{max}	E (au)	dim.	n_{max}	λ_{max}	E (au)
944	38	22	−0.5154	944	38	22	−2.8762	944	38	22	−21.890	944	38	22	−58.81
2626	86	20	−0.5205	2050	70	20	−2.8900	2050	70	20	−21.964	2050	70	22	−58.99
10 608	152	32	−0.5246	10 446	150	32	−2.8999	10 608	152	32	−22.009	10 446	150	32	−59.102
exact [62]			−0.5278	exact [63]			−2.9037	exact [62]			−22.031	exact [65]			−59.17

Table 5. Ground state energy E and maximum λ and l values and corresponding dimension (dim.) of the **A** matrix for bielectronic systems by truncation scheme of λ and l.

H^-					He					O^{6+}				
dim.	$n_{\max}$	$\lambda_{\max}$	$l_{\max}$	E (au)	dim.	$n_{\max}$	$\lambda_{\max}$	$l_{\max}$	E (au)	dim.	$n_{\max}$	$\lambda_{\max}$	$l_{\max}$	E (au)
330	40	20	0	−0.4251	420	40	38	0	−2.5715	306	34	32	0	54.00
582	40	20	2	−0.5060	422	42	12	2	−2.8021	860	34	32	6	−58.74
884	40	20	6	−0.5131	518	42	12	4	−2.8575	1006	34	32	10	−58.76
exact [62]				−0.5278	exact [63]				−2.9037	exact [65]				−59.17

Table 6. Ground state energy E and maximum λ and μ values and corresponding dimension (dim.) of the **A** matrix for bielectronic systems by truncation scheme of λ and μ.

H^-					He					O^{6+}				
dim.	$n_{\max}$	$\lambda_{\max}$	$\mu_{\max}$	E (au)	dim.	$n_{\max}$	$\lambda_{\max}$	$\mu_{\max}$	E (au)	dim.	$n_{\max}$	$\lambda_{\max}$	$\mu_{\max}$	E (au)
330	40	20	0	−0.4240	420	40	38	0	−2.5828	306	34	32	0	−54.98
582	40	20	4	−0.4962	422	42	12	4	−2.8302	860	34	32	12	−58.75
884	40	20	12	−0.5147	518	42	12	8	−2.8647	1006	34	32	20	−58.76
exact [62]				−0.5278	exact [63]				−2.9037	exact [65]				−59.17

Table 7. Ground state energy E and maximum λ values and corresponding dimension (dim.) of the **A** matrix for $e^-e^+e^-$ and H_2^+ by truncation scheme on λ.

$e^-e^+e^-$				H_2^+			
dim.	n_{max}	λ_{max}	E (au)	dim.	n_{max}	λ_{max}	p_0 (au)
1974	56	24	−0.2567	116	18	8	−1.1531
3624	75	28	−0.2582	516	40	12	−0.4111
exact [62]			−0.2620	exact [66]			1.0926

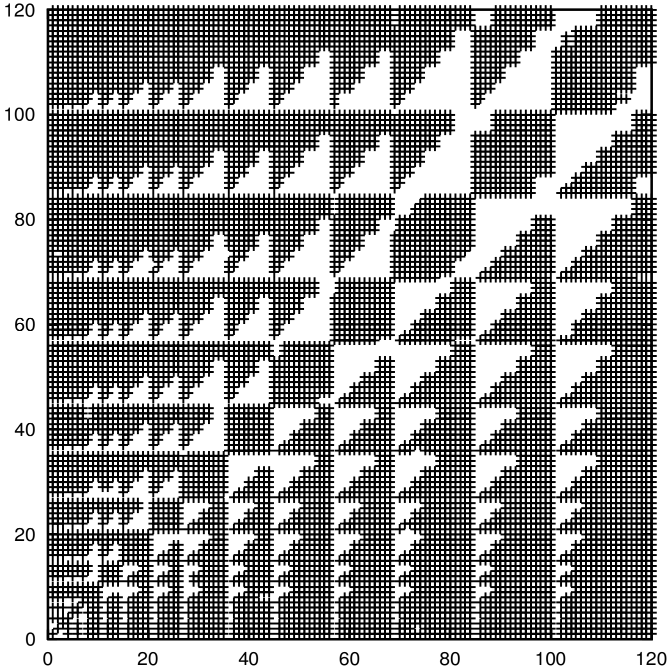
Table 8. Ground state energy E and maximum λ and μ for $e^-e^+e^-$ and H_2^+ by truncation scheme on λ and μ.

$e^-e^+e^-$					H_2^+				
dim.	n_{max}	λ_{max}	μ_{max}	E (au)	dim.	n_{max}	λ_{max}	μ_{max}	p_0 (au)
25	9	8	0	−0.2198	270	38	16	0	−0.6693
420	40	38	0	−0.2257	518	42	12	8	−0.4043
exact [62]				−0.2620	exact [66]				1.0926

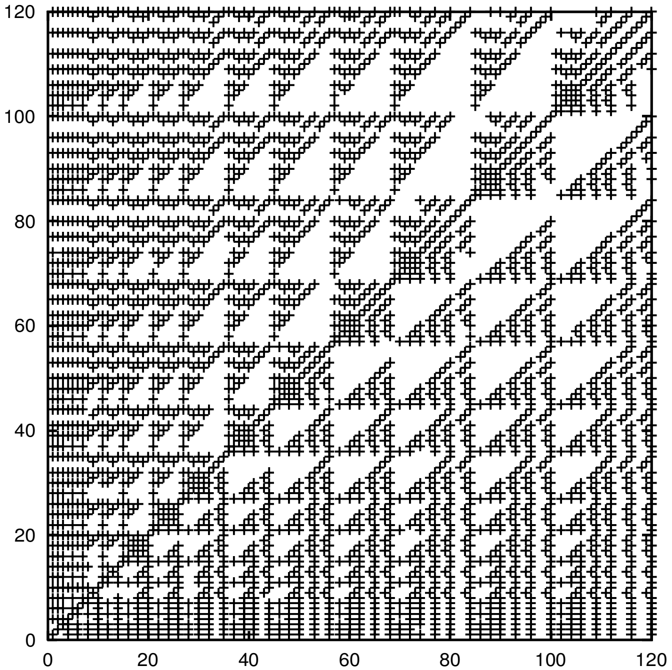
$-0.258\,231$ au was obtained for $\lambda_{max} = 24$, which is in agreement with the value one would get in the present approach by convergence on n for the same λ_{max}; indeed we found that for $n_{max} = 200$ we have $E = -0.258\,226$ au.

Truncation on the quantum number μ or l leads to slower convergence for the bielectronic series and this partially accounts for the poor performance for drastic cuts on λ. In both cases the truncation leads to similar results even if slightly better for a cut on μ. These characteristics become more pronounced as the charge increases, as can be seen from table 6, where only the limiting cases for the helium isoelectronic series have been reported. Further information about the different basis sets can be obtained analysing systems with a different mass ratio of the three particles. For $e^-e^+e^-$ (table 7) the behaviour is very similar to the case of helium, even if a better convergence is obtained by truncation on a higher value of λ ($\lambda = 28$). On the contrary for H_2^+ (table 7) a truncation only on λ does not lead to any improvement. Cutting on μ (table 8) is not worth it either, while the convergence becomes far more rapid by cutting drastically on l [55] (table 9).

As shown in figure 6(*a*) the matrix elements representing the coupling of states with values of l different from zero are notably smaller than those with $l = 0$ and can be neglected (i.e. an expansion set where $l = 0$ can be used). In figure 6(*b*) we illustrate the structure of the matrix $A_{nn'\lambda\lambda'\mu\mu'}$ and $A_{nn'\lambda\lambda'll'}$ which have been obtained by approximating to zero those elements whose value is four orders of magnitude smaller than the lowest eigenvalue. It can be seen that the residual elements obtained from the asymmetric hyperangular parametrization (with $l \neq 0$) are much more than those obtained from the symmetric parametrization, indicating that this basis set is more promising than a closed shell one. In figure 7 we also exhibit the structure of the matrix $A_{nn'\lambda\lambda'00}$: due to the presence of the zeroes of the radial integral the matrix structure becomes particularly compact and this feature can be exploited with the



(a)



(b)

Figure 6. Structure of the matrix $A_{nn'\lambda\lambda'\mu\mu'}$ (*a*) and $A_{nn'\lambda\lambda'll'}$ (*b*) for H_2^+, obtained considering all orbitals up to $n = 15$ (closed shell truncation scheme): elements more than four orders of magnitude smaller than the ground state eigenvalue are taken as zeroes. Matrix (*b*) is seen to be more sparse than matrix (*a*). The vanishing elements are those coupling states with $l \neq 0$. Thus the basis set with $l = 0$ results to be more rapidly converging than the closed shell one.

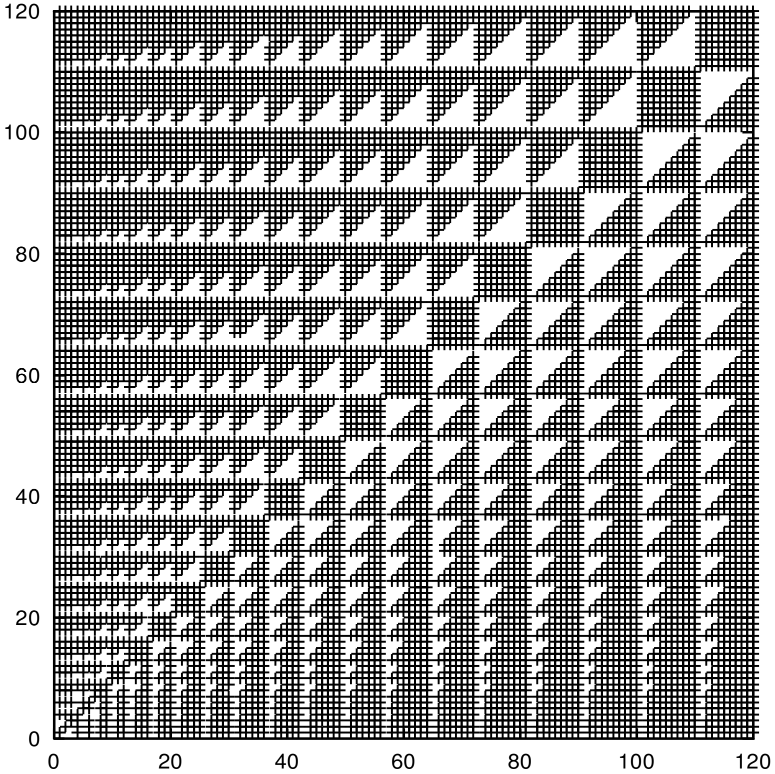


Figure 7. Matrix $A_{nn'\lambda\lambda'00}$ for H_2^+ with $n = 22$. It has the same structure as that of the $R_{nn'\lambda\lambda'}$ matrix and zero elements are more regularly distributed than for the matrix in figure 4.

Table 9. Ground state energy E and maximum λ and l for $e^-e^+e^-$ and H_2^+ by truncation scheme on λ and l.

$e^-e^+e^-$					H_2^+				
dim.	$n_{\max}$	$\lambda_{\max}$	$l_{\max}$	E (au)	dim.	$n_{\max}$	$\lambda_{\max}$	$l_{\max}$	p_0 (au)
25	9	8	0	−0.2061	270	38	16	0	−0.3290
420	40	38	0	−0.2069	1640	80	78	0	0.8080
					4290	130	65	0	0.9566
exact [62]				−0.2620	exact [66]				1.0926

application of diagonalization packages or algorithms (Lanczos, ARPACK) for sparse matrices [70]. The sparseness of these matrices is strictly linked to the behaviour of these basis sets under the parity operation. As we mentioned in section 2.2 parity conserving Sturmian basis sets corresponding to those described above are currently under investigation [32]. Their utilization, as well as the exploit of further unexplored yet discrete symmetries specific of the system under study, will be substantial in reducing the dimensions of the matrices to be diagonalized, thus

Table 10. Ground state energy E and maximum ν and l values for He and H_2^+ by truncation scheme on ν and l.

He					H_2^+				
dim.	$n_{\max}$	$\nu_{\max}$	$l_{\max}$	E (au)	dim.	$n_{\max}$	$\nu_{\max}$	$l_{\max}$	p_0 (au)
80	20	10	0	−2.5695	550	64	10	0	0.6181
420	30	12	10	−2.8549	550	60	11	0	0.6319
618	30	18	10	−2.8639	684	68	13	0	0.7067
exact [63]				−2.9037	exact [66]				1.0926

decreasing the computational load and the time requirements, which represent the main bottleneck in the practice of these calculations.

For helium (table 10) a truncation on ν is connected to a reduction on l, which does not appear to lead to good results. In any case, for the same values of l, λ seems to be a better quantum number with respect to ν. For the H_2^+ molecular ion the truncation on ν (table 10), even if not drastic, produces better results than a truncation on λ, so ν is certainly a better quantum number than λ. As a consequence the best basis for H_2^+ is that labelled by n, ν, l and we can remark that this can be understood by noting that ν and l are the principal quantum number and the orbital angular momentum of the hydrogen atom.

Regarding the alternative parametrization of section 3.3, the results presented here have to be considered as exploratory: having not succeeded so far in finding a sum rule for the connecting transformations, one has to store and multiply large matrices. This is an indication that there is need for further analytical developments that allow basis set transformations, and thus exploration of alternative truncation schemes.

4.2. *Further results and extensions*

In the past few years the utilization of basis sets described in this work, or their modifications and extensions, has found increasing attention for perspective applications to quantum systems in chemistry and physics. As a matter of fact these methods are an interesting and fruitful alternative to the usual self-consistent field approaches.

In this section we shall give a short list of applications of this kind (or of their modifications) to multielectronic bound systems (atoms and molecules) and to scattering problems, and their extensions to relativistic and to non-standard basis sets will be illustrated. The interested reader is referred to the reference list. Nuclear applications are covered by an extensive review [71].

For recent accounts of hyperspherical approaches to atomic structures as a few-body Coulomb problem, following the pioneering work of Fano, Macek and others, see references [72–76]. These authors investigated advantages of solving the problem parametrically in the hyperradius and then obtaining the spectra from bound states of adiabatic potential curves. Inclusion of non-adiabatic couplings by perturbation theory [69] has been reported.

Alternatives have been described regarding Coulomb Sturmians for many-electron systems: owing to the slow convergence of the previous ‘rigorous’ approach (section 3), other avenues have been pursued. Many-electron Sturmians have been constructed as the product of one-electron Sturmians [21–23, 77] and applied for extensive calculations of the energy spectrum of atoms and ions [78, 79] also in strong external fields [80, 81] where treatments based on perturbation theory are no longer applicable. Convergence of these sets is rapid, although the spectrum of the generating eigenproblem is mixed, containing also, apart from discrete eigenvalues, a continuum part: therefore there is no guarantee that every well-behaved function of the same variables obeying the same boundary conditions can be expanded in terms of this basis [82]. However [21], since if this extremely stringent condition were applied to the conventional many-electron basis sets actually used in configuration interaction calculations, all of them would be disqualified, great expectations are foreseen along these lines, which may amply exploit parts of well-developed quantum chemical codes.

An alternative approach, initially proposed by Fabre de la Ripelle for nuclear physics [83, 84] and developed essentially by Bian and Deng [85–87], called ‘potential harmonic’ method, consists of using selected ad-hoc subsets to obtain reasonable convergence for the three-body Coulomb problems (He atom, the positronium ion $e^+e^-e^+$, etc.).

The use of ad-hoc correlation functions of Jastrow type has also been proposed as successful in nuclear physics, where the ‘identity’ of nuclear particles (protons and neutrons) to solve problems up to eight nucleons is exploited (see [88–90] for recent extensions). However, both these methods are tailored only for calculations of ground state energies, and have to be adapted to give excited states, while in principle the procedure of sections 3 and 4.1 yields a whole spectral range.

As already mentioned, applications of Sturmian basis sets in momentum space to the description of molecular structure date back to 1965 when Shibuya and Wulfman [18] developed a treatment for the problem of one electron in the presence of many fixed nuclei by extending Fock’s momentum space method: in particular they applied this analysis to the H_2^+ molecular ion. The basic ingredient of their treatment is the explicit calculation of a matrix, usually indicated with $\mathbf{S}(R)$, representing the overlap between the basis eigenfunction relative to a certain nucleus and the eigenfunction basis set relative to another nucleus placed at an arbitrary distance. Monoelectronic energies and orbitals can be obtained, as shown elegantly by Dunlap [91], solving a secular problem involving only the $\mathbf{S}$ matrix. Further progress was made by other authors [92–94] and most important in this track is the work of Koga and co-workers [95–99] who, by using a secular equation based on the second iterated momentum space Schrödinger equation were able to obtain the electronic energy of H_2^+ with 10-figure accuracy as a function of the internuclear separation. The precision of their momentum space results at low values of $\mathbf{R}$ is higher than available configuration space calculations. The present authors [2] have extended Shibuya and Wulfman’s analysis using instead of conventional spherical orbitals, parabolic (or Stark) basis sets which provide a simpler expression for the $\mathbf{S}$ matrix and a better convergence when reduced basis sets are employed. The hypothesis of the approximate conservation of the parabolic quantum number leads to an eigenfunction expansion that, when truncated to only three orbitals, describes the electronic energy at the equilibrium state within 5%. One of the key points in Shibuya and Wulfman’s treatment is the introduction of a remarkable plane wave expansion in terms of hyperspherical harmonics and Coulomb Sturmians, extremely useful for molecular calculations. Extensions to the parabolic parametrization [2] and to the *d*-dimensional space [4], in view of multielectron molecular applications, have also been introduced by the present authors. The extension to many electron molecules is currently being studied [23].

Beside standard Sturmian basis sets recent advances have been made on elliptic orbitals (both sphero-elliptic and cylindrical-elliptic) coming from alternative separation of variables for the four dimensional sphere S^3. Despite the fact that their manipulation is more complicated, elliptic Sturmians have an additional degree of freedom, namely the modulus of Jacobi elliptic functions, measuring distances between elliptical foci: this makes them more flexible compared with standard Sturmians [32].

Relativistic Coulomb Sturmian basis sets have also been proposed and their properties discussed in [23, 100, 101] with reference to solving Dirac-type equations.

Beside atomic and molecular bound states, Sturmian basis sets have also been used to describe scattering processes. In [102] the generalized Sturmian method developed by Avery was applied to the inelastic scattering of fast electrons by atoms and ions. The approach is known to be fruitful for reactions involving three Coulomb particles, and applications so far have been devoted to muonic systems of interest in cold fusion [103–105]. Finally, in the work of our group concerning reactive scattering the slow convergence encountered for this type of set has been circumvented through the 'hyperquantization' algorithm based on discrete analogues of spherical and hyperspherical harmonics [62, 106]. For a recent review see [107]. Its implementation to the problems of interest here is a task for future work.

5. Conclusion

Our search for Sturmian expansion basis sets for atomic and molecular problems is triggered by the observation that conventional hydrogenoid *spherical* orbitals are strictly linked to tetradimensional harmonics on the hypersphere S^3 when the atomic orbitals for the tridimensional hydrogen atom are considered in momentum space. This encouraged us to study alternative representations such as those providing the *Stark* and *Zeeman* basis sets, related to the *spherical* one by orthogonal transformations, see equations (12) and (15). These transformations can also be interpreted as suitable *timber* coefficients relating different *tree* structures of hyperspherical harmonics for $\mathbf{R}^4$ (see figure 1).

The analysis of alternative representations for hydrogen atom wavefunctions can be extended to any mathematical dimension and therefore can be of interest beyond the one-electron case. The work in [5], outlined in section 3 suggests that what we have done there can also be exploited in higher dimensional problems [4]. In general, one has orthonormal basis sets seen from two complementary perspective viewpoints, the (hyper)harmonics and the (hyper)hydrogenoid position wavefunctions: since the multidimensional extension of Fock projection relates the harmonics to hydrogenoid momentum space wavefunctions, both can be used to expand the *d*-dimensional plane wave [4] and to Fourier transform between position and momentum space. Transformations between the generalizations to hyperspaces of the spherical and Stark bases similar to the one discussed in section 2 will require the introduction of generalized angular momentum coupling coefficients (Hahn and Racah polynomials), whose properties are described in [6, 41].

In configuration space, the many-body Coulomb problem, describing atomic and molecular structure, is isomorphic to that for a multidimensional hydrogen atom with an anisotropic charge [108]. This encourages (see [5]) multidimensional hydrogenoid Sturmian expansions [13, 109] consisting of a (hyper)radial part and of a hyperspherical harmonic. As outlined above, the corresponding eigenfunctions in momentum space are hyperspherical harmonics belonging to a space of one dimension higher. The calculation of matrix elements for the secular equation for the spectrum involves radial and angular integrals. Guided by the previous observation of the duality between multidimensional hydrogenoid Sturmians and hyperspherical harmonics, we have shown that not only angular integrals, but also radial ones can be obtained as (generalized) vector coupling coefficients and that the separation into radial and angular contribution disappears from the hyperspherical standpoint in momentum space.

Therefore, the numerical solution of the secular equation for different representations for three-body problems (section 4) enabled us to investigate the 'goodness' of the various quantum numbers arising in the labelling of the various kinds of harmonic. Alternative subgroup reduction chains corresponding to alternative expansions in hyperspherical harmonics, can also be dealt with by a generalization of angular momentum algebra [5]. Explicitly, as already noted, the three-body problem requires a mapping of the 6-sphere S^6 embedded in a seven dimensional Euclidean space. To test the effectiveness of the different parametrizations in some specific cases we have already illustrated the above considerations by some numerical examples again for the test case for H_2^+ [5, 54], but relaxing the usual restriction to the fixed nuclei scheme as adopted, for example in [2].

The generalization of the Fock stereographic projection of section 2 to $d \geq 3$ and in two alternative sets of hyperspherical angles is given in [4]. For alternative Sturmian basis sets (generalizations of the spherical and Stark Sturmians [2]), which enjoy the important properties of being complete and orthonormal sets in a d-dimensional configuration space [109, 110], following Shibuya and Wulfman [18] we can establish remarkable (hyper)-plane wave expansions of *the d-dimensional wave in a* $(d+1)$*-spherical harmonic and Sturmian hydrogenoid orbitals*. The mathematical aspects of such expansions for the $d = 3$ case are discussed in [110].

The extension to molecules starts from early work by Shibuya and Wulfman [18], who used an expansion of this type in momentum space for $d = 3$ to go on to expand one-electron molecular orbitals and to obtain secular equations for multicentre problems. Recently [2], the alternative orbitals corresponding to separation in parabolic coordinates were considered: in particular, the Stark basis was shown to be superior to the usual spherical basis for systems with axial symmetry, an important case study being the molecular orbitals for H_2^+ [2]. Further work will have to consider this also for multielectron orbitals, and the types of coordinates [32] insufficiently explored so far are worthy of closer attention.

In view of their optimal properties (orthonormality, completeness, discretization of the continuum) we expect multidimensional Sturmians (and their counterparts in momentum space) to be useful as expansion bases in a variety of atomic and molecular problems [1, 22]. An exploration of the use of six-dimensional Sturmians for two-electron systems (e.g. for the helium atom), exploiting alternative representations for seven-dimensional hyperspherical harmonics, has been first presented in [5] and documented in sections 3 and 4. (They may also be of interest for d-dimensional scaling problems [111].) It is shown there that many relevant matrix elements can accordingly be calculated by a generalized angular momentum algebra.

Indeed, the outstandingly attractive feature of the presently introduced Sturmian basis set, namely their identification with hyperspherical harmonics implies that physically, the labels of the harmonics can be considered as quantum numbers, and interpreted as associated to (hyper)angular momenta. So the mathematical apparatus of orthogonal polynomials and of special finite hypergeometric series can be taken over and given the physical interpretation of a generalized angular momentum algebra. An admittedly partial reference list includes [38, 41, 112, 113].

Several perspectives for future work open in the directions both of the development of such an algebra and of the quantum mechanical applications. Indeed special finite hypergeometric series (such as the Hahn polynomials encountered here (section 2)), which are generalizations of vector coupling coefficients [6], can be interpreted as discrete analogues of spherical and hyperspherical harmonics. This provided the tools required for the *hyperquantization technique* [70, 106], of interest for atomic and molecular problems, and developed by us for reactive scattering problems [107]. Analytical advances in this direction can foster progress in the numerical implementation of the hyperspherical harmonic approach to the solution of quantum chemical problems.

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